

**PCT**WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup> :</b> <b>A61K 7/06</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 98/48770</b> <b>(43) International Publication Date:</b> 5 November 1998 (05.11.98)
<b>(21) International Application Number:</b> PCT/US98/08347 <b>(22) International Filing Date:</b> 24 April 1998 (24.04.98)  <b>(30) Priority Data:</b> 08/843,104 25 April 1997 (25.04.97) US 08/939,847 29 September 1997 (29.09.97) US  <b>(71) Applicant:</b> THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US).  <b>(72) Inventors:</b> MIDHA, Sanjeev; Apartment 2, 9274 Deercross Parkway, Blue Ash, OH 45236 (US). BOLICH, Raymond, Edward, Jr.; 7201 Striker Road, Maineville, OH 45241 (US). JIVIDEN, Kathleen, Bridget; 2653 Timber Court, Lebanon, OH 45036 (US).  <b>(74) Agents:</b> REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217 (US).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> PERSONAL CARE COMPOSITIONS COMPRISING AN ADHESIVE COPOLYMER  <b>(57) Abstract</b>  The present invention relates to personal care compositions. These compositions comprise an adhesive copolymer and a solvent for the copolymer selected from the group consisting of water, ethanol, n-propanol, isopropanol, acetone, propylene glycol, and mixtures thereof. The compositions, when dried, exhibit a cohesive strength of greater than about 0.5 kgf/mm <sup>2</sup> , a total energy absorption per unit volume of greater than about 0.55 kgfmm/mm <sup>3</sup> , and an impact strength of greater than about 7000 ergs. Preferred air hairspray embodiments of the present invention having improved removeability from hair as defined by a hair stiffness value of from 0 to about 3.5 (0 to 4 scale) and a hair flaking value of from 0 to about 3.5 (0 to 4 scale), which values are determined by the removeability methodology defined herein.		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakhstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

## PERSONAL CARE COMPOSITIONS COMPRISING AN ADHESIVE COPOLYMER

TECHNICAL FIELD

The present invention relates to personal care compositions, especially to hair spray compositions having improved removeability from hair as defined by hair stiffness and flaking values. These compositions comprise an adhesive copolymer and a solvent for the copolymer selected from the group consisting of water, ethanol, n-propanol, isopropanol, acetone, propylene glycol, and mixtures thereof. The copolymer component, when dried, exhibits a cohesive strength of greater than about  $0.5 \text{ kgf/mm}^2$ , a total energy absorption per unit volume of greater than about  $0.55 \text{ kgfmm/mm}^3$ , and an impact strength of greater than about 7000 ergs.

BACKGROUND OF THE INVENTION

Personal care products play an important role in the life of most consumers. Personal care products cover a wide variety of products and forms and include shampoos, soaps, hair sprays, lotions, creams, antiperspirants, anti-acne products, nail enamels, lipsticks, foundations, mascaras, and sunscreens. Consumers are constantly seeking personal care products that provide the desired benefit sought and represent a good value.

Many personal care products use contain various resins, gums, and adhesive polymers. The polymers are used for a variety of purposes including thickening, feel properties, film-forming ability, active deposition, active penetration, hair holding, etc. Consequently there is constantly a search for developing polymers having improved properties for use in personal care products.

It has surprisingly been found in the present invention that adhesive copolymers having certain physical parameters are highly useful. These copolymers are used in combination with a solvent for the copolymer selected from the group consisting of water, ethanol, n-propanol, isopropanol, and mixtures thereof. The copolymer solvent mixtures, when dried, have a cohesive strength of greater than about  $0.5 \text{ kgf/mm}^2$ , a total energy absorption per unit volume of greater than about  $0.55 \text{ kgfmm/mm}^3$ , and an impact strength of greater than about 7000 ergs. Without being limited by theory, it is believed that these physical characteristics of the dried hair spray composition account for the benefits observed.

It has also been found that the preferred hair spray compositions of the present invention have an improved removeability from hair during shampooing, wherein the removeability is defined in terms of hair stiffness and hair flaking values ranging from 0

to about 3.5 (0 to 4 scale) These hair stiffness and flaking values are indirect measures of hair spray removeability. Each of these values are determined in accordance with the methodology defined herein.

It is therefore an object of this invention to provide personal care compositions comprising an adhesive copolymer and a solvent for the copolymer selected from the group consisting of water, ethanol, n-propanol, isopropanol, acetone, propylene glycol, and mixtures thereof.

It is another object of this invention to provide methods for treating skin or hair using these compositions.

It is another object of this invention to provide methods for styling and holding hair.

These and other objects will become readily apparent from the detailed description which follows.

#### SUMMARY OF THE INVENTION

The present invention relates to personal care compositions comprising:

- (a) an adhesive copolymer having a weight average molecular weight from about 10,000 to about 5,000,000, and
- (b) a solvent for said copolymer selected from the group consisting of water, ethanol, n-propanol, isopropanol, acetone, propylene glycol, and mixtures thereof, wherein said composition, when dried, has a cohesive strength of greater than about 0.5 kgf/mm<sup>2</sup>, a total energy absorption per unit volume of greater than about 0.55 kgfmm/mm<sup>3</sup>, and an impact strength of greater than about 7000 ergs. The compositions are preferably hair spray compositions having improved removeability, wherein removeability is defined by a hair stiffness value of from 0 to about 3.5 and a hair flaking value of from 0 to 3.5 (0 to 4 scale)

In further embodiments, the present invention relates to a method for treating the skin or hair by applying to the skin or hair an effective amount of a composition comprising,

a copolymer component comprising:

- (a) an adhesive copolymer having a weight average molecular weight from about 10,000 to about 5,000,000, and
- (b) a solvent for said copolymer selected from the group consisting of water, ethanol, n-propanol, isopropanol, and mixtures thereof, wherein said composition, when dried, has a cohesive strength of greater than about 0.5 kgf/mm<sup>2</sup>, a total energy absorption per unit volume of greater than about 0.55 kgf/mm<sup>2</sup>, and an impact strength of greater than about 7000 ergs. These methods are preferably



directed to the hair spray compositions of the present invention having the removeability values (hair stiffness values and hair flaking values) as defined herein.

#### BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 illustrates an overhead view of a dumbbell-shaped planar dried hair spray film sample useful for measuring the physical properties such as the cohesive strength and total energy absorption per unit volume as described herein.

Fig. 2 illustrates a cross-sectional view, showing the thickness of the dumbbell-shaped dried film illustrated in Fig. 1.

#### DETAILED DESCRIPTION OF THE INVENTION

The essential components of the present invention are described below. Also included is a nonexclusive description of various optional and preferred components useful in embodiments of the present invention.

The present invention can comprise, consist of, or consist essentially of any of the required or optional ingredients and/or limitations described herein.

All percentages and ratios are calculated on a weight basis unless otherwise indicated. All percentages are calculated based upon the total composition unless otherwise indicated.

All molecular weights are weight average molecular weights and are given in units of grams per mole.

All ingredient levels are in reference to the active level of that ingredient, and are exclusive of solvents, by-products, or other impurities that may be present in commercially available sources, unless otherwise indicated.

All measurements made are at ambient room temperature, which is approximately 73°F, unless otherwise designated.

All documents referred to herein, including all patents, patent applications, and printed publications, are hereby incorporated by reference in their entirety in this disclosure.

The term "suitable for application to human hair" as used herein, means that the compositions or components thereof so described are suitable for use in contact with human hair and the scalp and skin without undue toxicity, incompatibility, instability, allergic response, and the like.

The term kgf is a standard physical term denoting a kilogram of force subjected to gravitational acceleration, i.e.  $9.82 \text{ m/s}^2$ .

#### Adhesive Copolymer

The compositions of the present invention comprise from about 0.1% to about 30%, preferably from about 0.5% to about 20%, and more preferably from about 0.5% to about 10%, by weight of the composition, of an adhesive copolymer.

By "adhesive" is meant that when applied as a solution to a surface and dried, e.g., the hair or skin, the copolymer forms films or welds. Such a film or weld will have adhesive and cohesive strength, as is understood by those skilled in the art.

The copolymers, or salts thereof, of the present invention are soluble or dispersible in a solvent selected from the group consisting of water, ethanol, n-propanol, isopropanol, and mixtures thereof, at a concentration of at least about 0.1 mg/ml, preferably at least about 0.5 mg/ml, and more preferably at least about 1 mg/ml, at about 73°F.

The copolymers of the present invention have a weight average molecular weight, in grams/mole, of at least about 10,000. There is no upper limit for molecular weight except that which limits applicability of the invention for practical reasons, such as viscosity, processing, aesthetic characteristics, spreadability, formulation compatibility, etc. The weight average molecular weight is generally less than about 5,000,000, more generally less than about 2,500,000, and typically less than about 1,500,000. Preferably, the weight average molecular weight is from about 10,000 to about 5,000,000, more preferably from about 20,000 to about 1,000,000, even more preferably from about 30,000 to about 500,000, and most preferably from about 50,000 to about 300,000.

A wide variety of adhesive copolymers are useful in the present invention, provided the physical parameters of the dried hair spray film and the solubility or dispersibility requirements and the molecular weight requirements of the copolymer are met.

#### Adhesive Copolymers

The adhesive copolymers of the present invention are formed from the random copolymerization of vinyl monomer units and macromonomer units containing a polymeric portion and a vinyl moiety copolymerizable with vinyl monomer units. Upon completion of polymerization, the polymeric portion of the macromonomer units can form side chains of the copolymer. The vinyl monomer units and the vinyl moiety portion of the macromonomer units form the backbone. The vinyl monomer and the macromonomer can be selected from a wide variety of structures as long as the copolymer has the required properties described herein.

As will be clear to one skilled in the art, and especially from the Examples, the copolymer may have one or more side chains grafted to the backbone. In addition, the compositions of the present invention can include, in addition to the copolymer, low

levels of the corresponding copolymers having no side chains grafted to the backbone. As known in the art, synthetic graft copolymerization processes may produce a mixture of polymer molecules containing none, one, or more than one side chains covalently bonded to and pendant from the polymeric backbone. From knowledge of the amount and number average molecular weight of side chains in a polymer sample, and the number average molecular weight of the polymer sample, it is possible to calculate the average number of side chains per polymer backbone.

The grafted copolymers should satisfy the following two criteria:

- (2) the polymeric side chain portion is covalently bonded to the backbone portion; and
- (3) the number average molecular weight of the polymeric side chain portion is from about 1000 to about 50,000.

The copolymers of the present invention are prepared by the polymerization combination of vinyl monomers and macromonomers. The copolymers can be synthesized by free radical polymerization of the monomers and macromonomers. The general principles of free radical polymerization methods are well understood. See, for example, Odian, "Principles of Polymerization", 3rd edition, John Wiley & Sons, 1991, pp. 198-334. The desired vinyl monomers and macromonomers are all placed in a reactor, along with a sufficient amount of a mutual solvent so that when the reaction is complete the viscosity of the reaction is reasonable. Undesired terminators, especially oxygen, are removed as needed. This is done by evacuation or by purging with an inert gas, such as argon or nitrogen. The initiator is introduced and the reaction brought to the temperature needed for initiation to occur, assuming thermal initiators are used. Alternatively, redox or radiation initiation can be used. The polymerization is allowed to proceed as long as needed for a high level of conversion to be achieved, typically from a few hours to a few days. The solvent is then removed, usually by evaporation or by precipitating the copolymer by addition of a nonsolvent. The copolymer can be further purified, as desired.

As an alternative to a batch reaction, the copolymer can be made by a semi-continuous or continuous process. In the semi-continuous process, two or more additions of monomers or macromonomers are made during the polymerization reaction. This is advantageous when the copolymer is made of several monomers which react during the polymerization at different rates. The proportions of monomers added to the reaction at the separate points of addition can be adjusted by one of ordinary skill in the art such that the polymers of the final product have a more uniform structure. In other

words, the polymers of the final product will have a more consistent monomer content distribution for each of the monomer types charged to the reaction.

Examples of related copolymers and how they are made are described in detail in U.S. Patent 4,693,935, Mazurek, issued September 15, 1987, U.S. Patent 4,728,571, Clemens et al., issued March 1, 1988, both of which are incorporated herein by reference. Additional grafted polymers are also disclosed in EPO Application 90307528.1, published as EPO Application 0 408 311 A2 on January 11, 1991, Hayama, et al., U.S. Patent 5,061,481, issued October 29, 1991, Suzuki et al., U.S. Patent 5,106,609, Bolich et al., issued April 21, 1992, U.S. Patent 5,100,658, Bolich et al., issued March 31, 1992, U.S. Patent 5,100,657, Ansher-Jackson, et al., issued March 31, 1992, U.S. Patent 5,104,646, Bolich et al., issued April 14, 1992, U.S. Serial No. 07/758,319, Bolich et al., filed August 27, 1991, and U.S. Serial No. 07/758,320, Torgerson et al., filed August 27, 1991, all of which are incorporated by reference herein in their entirety.

The copolymers are prepared by the polymerization combination of vinyl monomers and macromonomers. The copolymer composition is characterized by the amount of each monomer charged to the polymerization reaction vessel, or alternatively used in a continuous or semi-continuous process.

By appropriate selection and combination of the particular vinyl monomer units and macromonomer units, and by the choice of specific relative ratios of the units well within the ability of one of ordinary skill in the art, the copolymers can be optimized for various physical properties and for compatibility with other ingredients commonly used in hair care applications.

Alternatively, the copolymers of the present invention can correspond to block type structures which can be described by the formulas A-B, A-B-A, and  $-(A-B)_n-$  wherein n is an integer of 2 or greater. A-B represents a diblock structure, A-B-A represents a triblock structure, and  $-(A-B)_n-$  represents a multiblock structure. The monomer units used to prepare these block copolymers are as described under the heading below.

#### Vinyl Monomer Units

The copolymers of the present invention comprise from about 50% to about 98%, preferably from about 60% to about 95%, and more preferably from about 70% to about 90% by weight of the vinyl monomer units. For the block copolymer, the vinyl monomer units can comprise 100%.

The vinyl monomer unit is selected from copolymerizable monomers, preferably ethylenically unsaturated monomers. Either a single type of vinyl monomer unit or combinations of two or more vinyl monomer units can be utilized. The vinyl monomers

are selected to meet the requirements of the copolymer. By "copolymerizable", as used herein, is meant that the vinyl monomer can be reacted with or polymerized with the polysiloxane macromonomers in a polymerization reaction using one or more conventional synthetic techniques, such as ionic, emulsion, dispersion, Ziegler-Natta, free radical, group transfer or step growth polymerization. In the present invention, monomers and macromonomers that are copolymerizable using conventional free radical initiated techniques are preferred. The term "ethylenically unsaturated" is used herein to mean a material that contains at least one polymerizable carbon-carbon double bond, which can be mono-, di-, tri- or tetra-substituted.

The monomer units can be derived from hydrophilic monomers (typically polar monomers), or mixtures of such hydrophilic monomers with hydrophobic monomers (typically low polarity monomers), provided that the solubility characteristics of the overall copolymer is achieved. As used herein, "hydrophilic monomers" means monomers which form homopolymers which are substantially water soluble; "hydrophobic monomers" means monomers which form substantially water insoluble homopolymers.

Nonlimiting classes of monomers useful herein include monomers selected from the group consisting of unsaturated alcohols, unsaturated monocarboxylic acids, unsaturated dicarboxylic acids, unsaturated anhydrides, alcohol esters of unsaturated monocarboxylic acids, alcohol esters of unsaturated dicarboxylic acids, alcohol esters of unsaturated anhydrides, alkoxylated esters of unsaturated monocarboxylic acids, alkoxylated esters of unsaturated dicarboxylic acids, alkoxylated esters of unsaturated anhydrides, aminoalkyl esters of unsaturated monocarboxylic acids, aminoalkyl esters of unsaturated dicarboxylic acids, aminoalkyl esters of unsaturated anhydrides, amides of unsaturated monocarboxylic acids, amides of unsaturated dicarboxylic acids, amides of unsaturated anhydrides, salts of unsaturated alcohols, salts of unsaturated monocarboxylic acids, salts of unsaturated dicarboxylic acids, unsaturated hydrocarbons, unsaturated heterocycles, and mixtures thereof.

Representative examples of such monomers include acrylic acid, methacrylic acid, N,N-dimethylacrylamide, dimethylaminoethyl methacrylate, quaternized dimethylaminoethyl methacrylate, methacrylamide, N-t-butyl acrylamide, maleic acid, maleic anhydride and its half esters, crotonic acid, itaconic acid, acrylamide, acrylate alcohols, hydroxyethyl methacrylate, diallyldimethyl ammonium chloride, vinyl pyrrolidone, vinyl ethers (such as methyl vinyl ether), maleimides, vinyl pyridine, vinyl imidazole, other polar vinyl heterocyclics, styrene sulfonate, allyl alcohol, vinyl alcohol (such as that produced by the hydrolysis of vinyl acetate after polymerization), vinyl

caprolactam, methacrylic acid esters of C<sub>1</sub>-C<sub>18</sub> alcohols, such as methanol, ethanol, methoxy ethanol, 1-propanol, 2-propanol, 1-butanol, 2-methyl-1-propanol, 1-pentanol, 2-pentanol, 3-pentanol, 2-methyl-1-butanol, 1-methyl-1-butanol, 3-methyl-1-butanol, 1-methyl-1-pentanol, 2-methyl-1-pentanol, 3-methyl-1-pentanol, t-butanol(2-methyl-2-propanol), cyclohexanol, neodecanol, 2-ethyl-1-butanol, 3-heptanol, benzyl alcohol, 2-octanol, 6-methyl-1-heptanol, 2-ethyl-1-hexanol, 3,5-dimethyl-1-hexanol, 3,5,5-trimethyl-1-hexanol, 1-decanol, 1-dodecanol, 1-hexadecanol, 1-octa decanol, and the like, the alcohols having from about 1-18 carbon atoms with the number of carbon atoms preferably being from about 1-12; dicyclopentenyl acrylate; 4-biphenyl acrylate; pentachlorophenyl acrylate; 3,5-dimethyladamantyl acrylate; 3,5-dimethyladamentyl methacrylate; 4-methoxycarbonylphenyl methacrylate; trimethylsilyl methacrylate; styrene; alkyl substituted styrenes including alpha-methylstyrene and t-butylstyrene; vinyl esters, including vinyl acetate, vinyl neononanoate, vinyl pivalate and vinyl propionate; vinyl chloride; vinylidene chloride; vinyl toluene; alkyl vinyl ethers, including isobutyl vinyl ether and s-butyl vinyl ether; butadiene; cyclohexadiene; bicycloheptadiene; 2,3-dicarboxymethyl-1,6-hexadiene; ethylene; propylene; indene; norbornylene;  $\beta$ -pinene;  $\alpha$ -pinene; salts of acids and amines listed above, and combinations thereof. The quaternized monomers can be quaternized either before or after the copolymerization with other monomers of the graft copolymer.

Preferred monomers include acrylic acid, methacrylic acid, N,N-dimethyl acrylamide, dimethylaminoethyl methacrylate, quaternized dimethylaminoethyl methacrylate, vinyl pyrrolidone, acrylic or methacrylic acid esters of C<sub>1</sub>-C<sub>18</sub> alcohols, styrene, alpha-methylstyrene, t-butylstyrene, vinyl acetate, vinyl propionate, 2-methoxyethyl acrylate, 2-ethoxyethyl acrylate, n-butyl methacrylate, isobutyl methacrylate, t-butyl acrylate, t-butyl methacrylate, 2-ethylhexyl methacrylate, methyl methacrylate, salts of any acids and amines listed above, and mixtures thereof.

#### Macromonomer Units

The copolymers of the present invention comprise from about 2% to about 50%, preferably from about 5% to about 40%, and more preferably from about 10% to about 30%, by weight of the copolymer of macromonomer units.

The macromonomer units are copolymerizable with the vinyl monomers, said macromonomers preferably having a vinyl moiety. Either a single type of macromonomer unit or combinations of two or more macromonomer units can be utilized herein. The macromonomers are selected to meet the requirements of the copolymer. By "copolymerizable", as used herein, is meant that the macromonomers can

be reacted with or polymerized with the vinyl monomers in a polymerization reaction using one or more conventional synthetic techniques, as described above.

The macromonomers that are useful herein contain a polymeric portion and a copolymerizable moiety which is preferably an ethylenically unsaturated moiety. Typically, the preferred macromonomers are those that are endcapped with the vinyl moiety. By "endcapped" as used herein is meant that the vinyl moiety is at or near a terminal position of the macromonomer.

The macromonomers can be synthesized utilizing a variety of standard synthetic procedures familiar to the polymer chemist of ordinary skill in the art. Furthermore, these macromonomers can be synthesized starting from commercially available polymers. Typically, the weight average molecular weight of the macromonomer is from about 1000 to about 50,000.

Preferred macromonomers are polyalkylene macromonomers. Polyalkylene macromonomers are exemplified by the general formula:



wherein I is an optionally present initiator (i.e.  $n = 0$  or  $1$ ), W is a monomer unit, E is an endcapping group, and m is an integer from about 10 to about 2000.

I is an optionally present chemical initiator moiety. Without being limited by theory, I can be derived from a chemical initiator or solvent used in the synthesis of the macromonomer. Nonlimiting examples of such initiators from which I can be derived include hydrogen ion, hydrogen radical, hydride ion, hydroxide ion, hydroxyl radical, peroxide radical, peroxide anion, C1-C20 carbocations, C1-C20 carbanions, C1-C20 carbon radicals, C1-C20 aliphatic and aromatic alkoxy anions, ammonium ion, and substituted ammonium ions (e.g., C1-C20 alkyl and C1-C20 alkoxy substituted), and mixtures thereof. I can be derived from any useful solvent, nonlimiting examples of which include water, methanol, ethanol, propanol, isopropanol, acetone, hexane, dichloromethane, chloroform, benzene, toluene, and mixtures thereof.

W is selected from one or more monomer units. Nonlimiting classes of such monomers include C1-C18 acrylate esters, C1-C18 methacrylate esters, C2-C30 straight and branched chain alkenes, styrenes, C1-C30 vinyl ethers, C4-C30 straight and branched chain dienes, and mixtures thereof.

Nonlimiting examples of W groups include those selected from the group consisting of t-butyl acrylate, acrylic acid, methacrylic acid, n-propyl methacrylate, isobutyl acrylate, n-butyl acrylate, dodecyl acrylate, ethyl acrylate, 2-ethylbutyl acrylate, n-heptyl acrylate, n-hexylacrylate, iso-butyl acrylate, iso-decyl acrylate, iso-propyl acrylate, 3-methylbutyl acrylate, 2-methylpentyl acrylate, nonyl acrylate, octyl acrylate,

1-propyl acrylate, 2-ethylhexyl methacrylate, octyl methacrylate, n-dodecyl methacrylate, n-octadecyl methacrylate, n-decyl methacrylate, n-pentyl methacrylate, isobutylene, isoprene, 1,2-butadiene, 1,3-butadiene, 5-methyl-1-hexene, 6-methyl-1-heptene, 4,4-dimethyl-1-pentene, iso-butyl vinyl ether, styrene, 2-methyl styrene, 3-methylstyrene, 4-methyl styrene, 2-t-butyl styrene, 3-t-butyl styrene, 4-t-butyl styrene, and mixtures thereof. A mixture of W units can be used herein. Additionally, these macromonomers can comprise polymers derived from the polymerization of acrylates, methacrylates, and other ethylenic moieties. The polymers derived from these W units can be selected for have either high ( $>25^{\circ}\text{C}$ ) or low  $T_g$  ( $\leq 25^{\circ}\text{C}$ ) values. The term  $T_g$  means glass transition temperature, which is familiar to one of ordinary skill in polymer science.

E is a copolymerizable moiety or "endcapping" group. Preferably E is an ethylenically unsaturated moiety. More preferred is when E is selected from the group consisting of vinyl, allyl, acryloyl, methacryloyl, ethacryloyl, 2-vinylbenzyl, 3-vinylbenzyl, 4-vinylbenzyl, 2-vinylbenzoyl, 3-vinylbenzoyl, 4-vinylbenzoyl, 1-butenyl, 1-propenyl, isobutenyl, cyclohexenyl, cyclopentenyl, and mixtures thereof. Even more preferred is when E is selected from the group consisting of vinyl, allyl, acryloyl, methacryloyl, ethacryloyl, 3-vinylbenzyl, 4-vinylbenzyl, 3-vinylbenzoyl, 4-vinylbenzoyl, 1-butenyl, 1-propenyl, isobutenyl, and mixtures thereof. Most preferred is when E is selected from the group consisting of vinyl, allyl, acryloyl, methacryloyl, ethacryloyl, 3-vinylbenzyl, 4-vinylbenzyl, and mixtures thereof.

Nonlimiting examples of macromonomer units useful herein include those selected from the group consisting of acryloyl, methacryloyl, or 3-, or 4-vinylbenzyl endcapped polymers of poly(n-butyl acrylate), poly(dodecyl acrylate), poly(2-ethylhexyl acrylate), poly(2-ethylbutyl acrylate), poly(n-ethyl acrylate), poly(n-heptyl acrylate), poly(n-hexyl acrylate), poly(iso-butyl acrylate), poly(iso-decyl acrylate), poly(iso-propyl acrylate), poly(3-methylbutyl acrylate), poly(2-methylpentyl acrylate), poly(nonyl acrylate), poly(octyl acrylate), poly(propyl acrylate), poly(2-ethylhexyl methacrylate), poly(tridecyl methacrylate), poly(hexyl methacrylate), poly(decyl methacrylate), poly(octyl methacrylate), poly(octadecyl methacrylate), poly(dodecyl methacrylate), poly(n-pentyl methacrylate), poly(isobutylene), poly(isoprene), hydrogenated poly(1,2-butadiene), hydrogenated poly(1,4-butadiene), hydrogenated poly(isoprene), poly(1,2-butadiene), poly(1-butene), poly(5-methyl-1-hexene), poly(6-methyl-1-heptene), poly(4,4-dimethyl-1-pentene), poly(iso-butyl vinyl ether), poly[4-t-butyl vinyl benzene-co-2-ethylhexyl acrylate], poly[2-ethylhexyl acrylate-co-octyl acrylamide], poly[2-ethyl



vinyl benzene-co-octyl methacrylate)], poly(n-propyl methacrylate-co-methacrylic acid), and mixtures thereof.

#### Neutralized Copolymers

As is known in the art, polymers which have acidic functionalities, such as carboxyl groups, are usually used in at least partially neutralized form to promote solubility/dispersibility of the polymer. In addition, use of the neutralized form aids in the ability of the dried compositions to be removed from the hair or skin. When neutralized, it is preferred that from about 10% to 100%, more preferably from about 20% to about 90%, and even more preferably from about 40% to about 85%, of the acidic monomers of the copolymer be neutralized.

Any conventionally used base, including organic or inorganic (metallic or other) bases, can be used for neutralization of the polymers. Metallic bases are particularly useful in the present compositions. Hydroxides, where the cation is ammonium, an alkali metal or an alkaline earth metal, are suitable neutralizers for use in the present compositions. Preferred neutralizing agents for use in compositions of the present invention are potassium hydroxide and sodium hydroxide. Examples of other suitable neutralizing agents which may be included in the compositions of the present invention include amines, especially amino alcohols such as 2-amino-2-methyl-1,3-propanediol (AMPD), 2-amino-2-ethyl-1,3-propanediol (AEPD), 2-amino-2-methyl-1-propanol (AMP), 2-amino-1-butanol (AB), monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA), monoisopropanolamine (MIPA), diisopropanolamine (DIPA), triisopropanolamine (TIPA) and dimethyl stearamine (DMS). Particularly useful neutralizing agents are mixtures of amines and metallic bases.

Polymers having basic functionalities, e.g., amino groups, are preferably at least partially neutralized with an acid, e.g., hydrochloric acid.

Neutralization can be accomplished by techniques well known in the art, and before or after polymerization of the monomers comprising the graft copolymer.

Solubility of the copolymer, as described above, should be determined after neutralization, if any, as well as after addition of other ingredients that may be included in the copolymer/solvent systems.

#### Preferred Polymers Of The Present Invention

Nonlimiting examples of preferred polymers of the present invention include those selected from the group consisting of poly[(t-butylacrylate-co-n-butylacrylate-co-acrylic acid)-graft-poly(t-butylacrylate-co-acrylic acid)-graft-[poly(isobutylene)]], poly(4-t-butylstyrene-co-methacrylic acid)-graft-[poly(isobutylene)], poly[(t-butylstyrene-co-methacrylic acid)-graft-[poly(2-ethylhexyl methacrylate)]], poly[(t-

butylacrylate-co-2-methoxyethyl acrylate-co-methacrylic acid)]-graft[poly(n-propyl methacrylate-co-methacrylic acid)], poly[(t-butylacrylate-co-2-methoxyethyl acrylate-co-methacrylic acid)]-graft-poly(n-propyl methacrylate-co-acrylic acid)], poly[(t-butylacrylate-co-2-methoxyethyl acrylate-co-methacrylic acid)]-graft-[poly(styrene-co-methacrylic acid)], and mixtures thereof.

Nonlimiting examples of preferred polymers of the present invention include those selected from the group consisting of poly[(t-butylacrylate-co-2-methoxyethyl acrylate-co-methacrylic acid)]-graft-poly(n-propyl methacrylate-co-methacrylic acid).

More specific examples of copolymers of the present invention include the following, where the composition is given as weight percentage of each monomer used in the polymerization reaction (i.e. the weight percentage of the monomers and macromonomers charged).

poly(t-butylacrylate-co-2-methoxyethylacrylate-co-acrylic acid)-graft-[poly(n-propyl methacrylate-co-methacrylic acid)] having a weight average molecular weight of about 150,000, comprising about 22% t-butylacrylate, 42% 2-methoxyethylacrylate, 18% acrylic acid, 18% poly(n-propylmethacrylate-co-methacrylic acid) macromonomer with a weight average molecular weight of about 6000.

poly[(t-butylacrylate-co-2-methoxyethyl acrylate-co-acrylic acid)-graft-[poly(isobutylene)]] having a weight average molecular weight of about 200,000, comprising about 40% t-butylacrylate, 20% n-butylacrylate, 20% acrylic acid, with a molecular weight of about 10,000, and 20% poly(isobutylene) macromonomer with a molecular weight of about 4,000..

### Solvent

The compositions of the present invention comprise from about 70% to about 99.9%, preferably from about 75% to about 98%, and more preferably from about 85% to about 98%, by weight of the composition, of a solvent for the copolymer. The solvent is selected from the group consisting of water, ethanol, n-propanol, isopropanol, and mixtures thereof.

Where water and alcohol mixtures are used, for instance, water-ethanol or water-isopropanol-ethanol, the water content of the compositions is generally in the range of from about 0.5% to about 99%, preferably from about 5% to about 50%, by weight of the total composition. In such mixtures, the alcohol solvents are generally present in the

range of from 0.5% to about 99%, preferably from about 50% to about 95%, by weight of the total composition.

In yet another aspect of this invention are provided hair spray compositions which contain reduced levels of volatile organic compounds such as solvents. As used herein, "volatile organic compounds" or "VOCs" are those organic compounds that contain less than 12 carbon atoms or have a vapor pressure greater than about 0.1 mm of mercury. A reduced volatile organic compound hair spray composition of the present invention contains no more than 80% volatile organic compounds.

#### Properties Of The Dried Copolymer Component

The copolymer component of the personal care compositions of the present invention, when dried, have specific physical properties as defined by the cohesive strength and total energy absorption per unit area. The dried copolymer components also exhibit specific impact strength properties, and when used in the preferred hairspray embodiments of the present invention have an improved removeability as defined in terms of hair stiffness and flaking values.

#### Cohesive Strength (kgf/mm<sup>2</sup>)

Cohesion is the strength of the bonds formed within a sample, e.g., a dried hair copolymer solvent composition. The cohesive strength, which is designated as kgf/mm<sup>2</sup> (kilograms of force per square millimeter) is the maximum unit stress a material will withstand when being subjected to displacement in tension. Stress is the ratio of measured load (kg X f) to the original cross-sectional area (mm<sup>2</sup>) of the sample.

The cohesive strength of the dried copolymer components of the current invention are determined using the following method. This method is based on ASTM Designation: D 638-91, Standard Test Method for Tensile Properties of Plastics, Published January 1992, herein incorporated by reference in its entirety. The following test method to measure cohesive strength is similar to the ASTM standard, however, several modifications are made to better represent the tensile properties of the dried films. The measurements are made at about 73°F and about 50% relative humidity. The test method, described herein specifically uses a modified dumbbell shape with a thickness equal to about 0.4 mm., and uses an Instron Model Mini-55 (available from Instron Corporation, Canton, MA) as the testing machine for applying the force to the polymer film samples.

A dried film sample is prepared by drying an amount of the hair spray composition (i.e., the silicone-containing adhesive copolymer and solvent selected from the group consisting of water, ethanol, n-propanol, isopropanol, and mixtures thereof, and any

additional optional components) in a flat-bottomed aluminum mold coated with PFA (perfluoroalkoxy) Teflon®. The copolymer film is dried at about 73°F and about 50% relative humidity until film has attained a "constant weight". By "constant weight" is meant that there is less than a 1% weight fluctuation in the sample over a period of 24 hours. The drying film should be kept in an area protected from air currents, which could result in non-uniform drying and formation of air bubbles. The copolymer film is cut into a dumbbell shape for testing. The sample should be substantially free of defects, i.e. cracks, chips, tears, etc. Figures 1 and 2 illustrate the planar dumbbell shaped film to be used in the tensile testing described herein for the cohesive strength and the total energy absorption per unit volume. Figure 1 illustrates an overhead view of the dumbbell shaped sample. Figure 2 illustrates a cross section through the dumbbell shaped sample. The width of the narrow section, 1, of the dumbbell is about 3 mm (1 = 3 mm). The length of the narrow, 3 mm., section of the dumbbell, 3, is about 13 mm. (3 = 13 mm.). The gauge length of the narrow section, 2, is the initial film length used in the determination of the strain of the sample. The gauge length is equal to or less than the length of the narrow section, preferably equal to the length of the narrow section (i.e., 2 = 3). The width of the ends of the dumbbell, 4, are about 10 mm. (4 = 10 mm.). The distance between end sections of the film, 5, is about 28 mm. (5 = 28 mm.). The overall length of the film, 6, is about 64 mm. (6 = 64 mm.). The length of the wide ends of the film is about 18 mm. ( $(6-5)/2 = 18$  mm.). The transition sections between the wide ends and the narrow section of the film are about 6.5 mm. in length (i.e.  $(5-3)/2 = 6.5$  mm.). Also the end portions of the narrow, center portion should be smoothly curved to avoid any stress points in the sample. The curve of the transition section, should have a radius, 7, of from about 0.5 in. to about 5 inches, and should join tangentially to the narrow section. The film is formed to a thickness, 8, of 0.4 mm. (8 = 0.4 mm.). The dumbbell shaped samples are further equilibrated to a "constant weight". By "constant weight" is meant that over a selected 4 day period, there is no more than 0.2% average weight gain or loss, relative to the dumbbell's measured weight 4 days previous and no more than  $\pm 0.2\%$  weight drift should be observed between two consecutive measurements in the four day period of time. The dumbbell should be tested within a 7 day period of reaching this constant weight.

The samples are tested on a calibrated Instron Model Mini-55 tensile tester. Before mounting the sample into the Instron, the length, 3, width, 1, and thickness, 8, of the narrow section of the dumbbell shaped sample are measured to the nearest micron with a calibrated micrometer. The dimensional measurements are required by the Instron for force per unit area calculations. The wide ends of the dumbbell samples are clamped into

the Instron and pulled at a crosshead rate of 5 mm. per minute. The Instron tester measures the overall forces (e.g., kgf) applied to the film. These forces are spread over the cross sectional area of the narrow section of the film. The cohesive strength of the copolymer is the maximum unit force measured by the Instron divided by the cross sectional area of the narrow portion of the film

The dried copolymer component of the compositions of the present invention have a cohesive strength of greater than about 0.5 kgf/mm<sup>2</sup>, preferably greater than about 0.6 kgf/mm<sup>2</sup>, and more preferably greater than about 0.7 kgf/mm<sup>2</sup>.

#### Total Energy Absorption Per Unit Volume (e.g., kgfmm/mm<sup>3</sup>)

The total energy absorption per unit volume, which is designated as kgfmm/mm<sup>3</sup> (kilograms of force millimeters per millimeter cubed), is the ratio of the total energy required to reach the autobreak point (in kgf X mm) to the original volume of the sample (mm<sup>3</sup>). The total energy required to reach the break point is calculated using standard techniques by determining the area under a load versus displacement curve for the sample. The total energy absorption per unit volume is also known as "toughness" by those skilled in the art of polymer science and materials testing.

The measurements are made at about 73°F and about 50% relative humidity.

The dried copolymer component of the compositions of the present invention have a total energy absorption per unit volume of greater than about 0.55 kgfmm/mm<sup>3</sup>, preferably greater than about 0.75 kgfmm/mm<sup>3</sup>, more preferably greater than about 1.10 kgfmm/mm<sup>3</sup>, more preferably greater than about 1.60 kgfmm/mm<sup>3</sup>, and most preferably greater than about 2.15 kgfmm/mm<sup>3</sup>.

#### Impact Strength

Impact strength is the mean-failure energy (mass X gravity X height) required to produce sample failure, e.g., in a dried hair spray composition. The sample failure is characterized by a crack or split created by the impact of the falling weight that can be seen by the naked eye under normal laboratory lighting conditions.

The impact strength of the dried copolymer components of the compositions of the current invention are determined using the following method. This method is based on ASTM Designation: D 5420-93, Standard Test Method for Impact Resistance of Flat, Rigid Plastic Specimen by Means of a Striker Impacted by a Falling Weight (Gardner Impact), Published 1995, herein incorporated by reference in its entirety, however, several modifications are made to better represent the impact properties of the dried film. The measurements are made at about 73°F and about 50% relative humidity.

The test method, described herein specifically uses rectangular shaped samples with a thickness equal to about 0.4 mm, and uses a GCA/Precision Scientific Penetrometer modified to drop a blunt faced probe to a distance of 70 mm and equipped with a Precision Scientific solenoid controller for GCA Penetrometer, a blunt faced cylindrical probe with a surface area of 8 mm<sup>2</sup> (OK M&T Corp. - part# WSU30), and a ruler which measures in 1 mm increments.

The samples are prepared using the film drying method described above in the cohesive strength measurements. The copolymer film is cut into the rectangular shape, e.g. 10 mm X 20 mm. The thickness of the sample is 0.4 mm. The film thickness of various test samples should be maintained within  $\pm 15\%$  of 0.4 mm.

The following measurement process is used. Turn on the solenoid operated probe release controller. The controller should begin to cycle on and off as indicated by a red light. Be sure the probe face is flush with the impact surface so that the sharp edge of the probe does not strike the film. Place a film sample on the Impact Tester over the target area. Direct the metric ruler gently on the film sample. Direct the lightening source across the surface of the sample such that the light source is in the same plane as the surface of the film. Small fractures in the film will reflect light and be easily detected. Move the probe up to desired drop distance. A suggested distance progression is: 1 mm, 3 mm, 5 mm, 10 mm, 15 mm, 20 mm, 25 mm, and further 5 mm increments up to 70 mm. (70 mm is the upper limit of the instrument). Turn on the instrument switch, to drop the probe onto the sample. The first step in the measurement of impact energy is to find the range of probe height necessary to fracture the film. Start at 1 mm for the first step. Continue to move up according to the suggested distance progression until a fracture is observed. When a fracture is observed make a note of it and move to a new sample. The second step in determining impact energy is to set a new sample and start drop at an observed fracture point in the range procedure. Set a new film sample and move the probe to the next lowest setting. If the film fractures, record result and repeat previous step. If the film does not fracture, set a new sample and move to the next distance. Continue to set new samples and increase the drop distance until the film fractures. Continue the procedure until 5 fractures are observed. Calculate the amount of work energy, i.e. the fracture strength using the following formula:

$W = m \times g \times h$ , where

W = amount of work energy in ergs,

m = mass of probe (59.53 g) (The probe is removable and can be replaced with one of different mass or impact surface area).

g = gravitational constant (980.665 cm/sec<sup>2</sup>),

$h$  = average distance probe travels to impact (cm).

The dried hair spray compositions of the present invention have an impact strength of greater than about 7000 ergs, preferably greater than about 20,000 ergs, and more preferably greater than about 50,000 ergs.

#### Hair Spray Removeability

The adhesive copolymers herein have improved removeability when used in the preferred hairspray embodiments of the present invention. In this context, removeability means that the adhesive copolymers are more easily removed from the hair or other applied surface during shampooing.

For purposes of defining the preferred hair spray compositions of the present invention, removeability is determined indirectly by evaluating hair stiffness and the appearance of observable white flakes after treating the hair in accordance with the removeability methodology described hereinafter. It has been found that the removeability of a hair spray formulation after shampooing correlates with the resulting stiffness/softness of the hair and the appearance/nonappearance of white flakes on the hair after a series of shampooing cycles. The hair spray compositions of the present invention have high removeability e.g., reduced stiffness and reduced white flaking. The term "removeability" as used herein therefore refers to hair stiffness values (0-4 scale) and white flaking values (0-4 scale) as measured in accordance with the methodology described hereinafter.

For purposes of the defining the preferred hair spray compositions of the present invention, the removeability of the hair spray compositions is defined as a combination of hair stiffness values and hair flaking values, wherein the hair spray compositions provide hair flaking values ranging from 0 to about 3.5, preferably from 0 to about 2.5, more preferably from 0 to about 2.0, and hair stiffness values ranging from 0 to about 3.5, preferably from 0 to about 2.5, more preferably from 0 to about 2.0.

#### Methodology: Hairspray Removeability

Removeability of the hairspray composition of the present invention, as indirectly evaluated in terms of hair stiffness and the appearance of white flakes, is determined in accordance with the following methodology. The methodology simulates multiple application and multi-cycle application of hairspray compositions so as to indirectly determine how readily and effectively such hairspray compositions are removed from hair.

The methodology described herein provides a means of evaluating hair switches blindly treated with hairspray embodiments of the present invention. The method by which each hair switch is treated with the hairspray embodiments, and the method by which each treated hair switch is then evaluated for removeability are described in detail below.

Two trained panelists each evaluate identically treated hair switches or sets of hair switches for stiffness and the appearance of white flakes. The panelists then individually assign each of the treated hair switches with a numerical score (0 to 4 scale) for hair stiffness and a numerical score for flaking (0 to 4 scale). The order in which the hair switches are treated with different hair spray embodiments is randomized and conducted round robin. Two identical sets of switches are prepared as described below for each panelist so that each has a fresh set of switches to evaluate. Before evaluating the blindly treated hair switches, each panelist also evaluates (not blinded) an untreated hair switch as a zero reference for hair stiffness and flaking. Each panelist also evaluates a control treated hair switch as a flaking reference (score 4.0) and another control treated hair switch as a hair stiffness reference (score 4.0). The hair stiffness values as defined herein are determined by averaging the hair stiffness scores provided by the two panelist. Likewise, the hair flaking values as defined herein are determined by averaging the hair flaking scores provided by the two panelists.

The hair switches are treated with either an aerosol or non-aerosol hair spray embodiment of the present invention in accordance with the following steps. The hair stiffness reference and the flaking reference are also prepared in accordance with the following steps, except that each is treated with the corresponding hair spray formulations as described hereinafter in Tables 2 and 3.

- 1) Vertically suspend a clean hair switch (10 inch European virgin brown hair, 20 gram) from its bound end and comb (black rubber comb, 5 inches by 1 inch, 1/2 fine tooth) through the switch to remove any tangles.
- 2) If necessary, use a static gun to eliminate any static build-up on the switch.
- 3) For non-aerosol products, spray the switch from a distance of 4 inches while applying ten pumps of the product to the switch and while moving the atomized spray pattern in a fluid up-and-down motion to cover the entire switch, or for aerosol products, spray each switch from a distance of 6 inches while applying the aerosol stream to the switch for a period of 3 seconds and while moving the aerosol stream in a fluid up-and-down motion to cover the entire switch.
- 4) Repeat step 3 on the opposite side of the switch.



- 5) After spraying the opposite side of the switch, hang the treated switch from its bound end to allow it to dry for one hour at ambient temperature, pressure and humidity.
- 6) Comb the dried switch using a black rubber comb (5 inches x 1 inch, 1/2 inch fine tooth) by combing away from the bound end of the switch but by initially starting toward the unbound end taking smaller strokes and then gradually taking larger strokes until the comb passes through the entire unbound length of the treated switch.
- 7) Repeat steps 1 through 6.
- 8) Wet the treated hair switch with water (+15-20 grain hardness, 38°C, 1 gal/min. water pressure).
- 9) Apply 1 ml of shampoo ( Table 1: methodology shampoo) along the length of the front of the wet hair switch and apply another 1 ml of the shampoo along the length of the reverse side of the wet hair switch.
- 10) Gently milk the switch from top to bottom (hand over hand between thumb and fingers) for 15 seconds at 1 stroke per second.
- 11) Rinse the hair switch with water (38°C, +15-20 grain hardness, 1 gal/min. water pressure) for 15 seconds. Gently squeeze the hair between the first and second fingers, drawing the fingers down the switch after 5 seconds, 10 seconds, and after final rinse.
- 12) Hang the treated switch and allow it to dry for two hours at 60°C in a hot box.
- 13) Remove the dried switches from the hot box.
- 14) Comb the dried switch using a black rubber comb (5 inches x 1 inch, 1/2 inch fine tooth) by combing away from the bound end of the switch but by initially starting toward the unbound end taking smaller strokes and then gradually taking larger strokes until the comb passes through the entire unbound length of the treated switch.
- 15) Repeat steps 1-14.
- 16) Repeat steps 1-13.
- 17) A panelist then evaluates the treated switch by feeling it between their first and second fingers of their dominant hand and between their thumb and other fingers for stiffness and resistance to bending, and then assigns to the treated switch a hair stiffness score (0 to 4 scale). The value of the assigned score is relative to the hair stiffness reference score (4) and the untreated reference score (0).
- 18) The panelist then combs the evaluated switch in accordance with the procedure set forth in Step 14 above, and then visually evaluates the combed switch for

white flakes, coating, and white haze and assigns it a hair flaking score (0 to 4 scale). The value of the assigned score is relative to the hair flaking reference score (4) and the untreated reference score (0).

Table 1: Methodology Shampoo

Ingredient List	Percent Composition As Added	Percent Composition Chemical Content
Sodium Laureth Sulfate	40.0000	10.0000
Water - USP Purified	30.3000	30.3000
Sodium Lauryl Sulfate	29.1000	8.0025
Cocamide DEA	.5000	.4000
Kathon CG	.1000	.0015
Citric Acid Solution (50% active)	** adj. from 0 - 1% (note: water level qs. to 100%)	

Table 2: High Flaking Control

Raw Materials	Percent Composition As Added	Percent Composition Chemical Content
Octylacrylamide/Acrylates/Butylaminoethyl Methacrylate Copolymer (National Starch lot AF-6713)	4.50	4.50
Water - USP Purified	15.50	15.50
Ethanol (SDA 40)	80.00	80.00

Table 3: High Stiffness Control

Raw Materials	Percent Composition As Added	Percent Composition Chemical Content
Octylacrylamide/Acrylates/Butylaminoethyl Methacrylate Copolymer (National Starch lot AF-6713)	6.00	6.00
Aminomethylpropanol, 95%	1.04	0.99
Water - USP Purified	15.50	15.50
Diisobutyl Adipate	0.20	0.20

Ethanol (SDA 40)	80.00	80.00
------------------	-------	-------

Each of the formulations described in Tables 1-3 are prepared by conventional formulation and mixing techniques.

#### Optional Ingredients

The compositions of the present invention can also comprise a wide variety of optional ingredients that are suitable for application to human hair.

The compositions hereof can optionally contain a plasticizer for the copolymer. Any plasticizer suitable for use in hair care products or for topical application to the skin or hair can be used. A wide variety of plasticizers are known in the art. These include glycerin, diisobutyl adipate, butyl stearate, propylene glycol, tri-C<sub>2</sub>-C<sub>8</sub> alkyl citrates, including triethyl citrate and tri-propyl, -butyl, -pentyl, etc., analogs of triethyl citrate. Triethyl citrate is preferred.

Plasticizers are typically used at levels of from about 0.01% to about 10%, by weight of the composition, preferably from about 0.05% to about 3%, more preferably from about 0.05% to about 1%. Preferably, the weight ratio of graft copolymer to the plasticizer is from about 1:1 to about 40:1, preferably from about 2:1 to about 30:1, more preferably from about 3:1 to about 25:1.

Optionally, the compositions of the present invention can contain an effective amount of a non-surface active ionic strength modifier system for reducing the viscosity of the hair spray composition. When used, the ionic strength modifiers will be present in the present compositions at a level of at least about 0.01%, by weight of the composition. The upper limit is dependent upon the maximum amount of the ionic strength modifiers that can be present in the particular compositions hereof such that the hair setting resin remains solubilized or dispersed. As will be understood by those skilled in the art, as the ionic strength of the composition is increased, the resin will eventually fall out of solution, or otherwise no longer remain solubilized or dispersed in the hydrophilic liquid carrier. The upper limit of the ionic strength modifier system level will vary depending upon the particular ionic strength modifiers, liquid vehicle, resin, and other ingredients present in the composition. Thus, for example, the maximum amount of the ionic strength modifiers that can be used will tend to be lower for compositions with liquid vehicles containing less water, compared to compositions with more water. Generally, the compositions will comprise about 4%, by weight, or less of the ionic strength modifiers, more generally about 2% or less, and typically about 1% or less. Preferably, the compositions hereof will comprise from about 0.01% to about 0.5%, more preferably from about 0.01% to about 0.1%, of the ionic strength modifier system.

The ionic strength modifier system comprises a mixture of monomeric cations and anions. The ions of the ionic strength modifier system hereof are non-surface active, i.e. they do not significantly reduce surface tension. For purposes hereof, non-surface active shall mean the ions, which at a 0.5% aqueous solution concentration, reduce surface tension by no more than 5.0 dynes/cm<sup>2</sup>. Generally, the ions of the ionic strength modifier system hereof will be characterized by having, at maximum, four or less carbon atoms per charge, preferably two or less carbon atoms, in any aliphatic chain or straight or branched chain organic heterochain.

The ionic strength modifier system comprises monomeric ions of the type which are products of acid-base reactions. Thus, basic and acidic ions OH<sup>-</sup> and H<sup>+</sup> do not constitute part of the ionic strength modifier system hereof, although they may be present in the composition. The ions hereof are incorporated into the composition in a form such that they can exist in the composition as free ions, i.e., in dissociated form. It is not necessary that all of the ions added exist in the composition as free ions, but must be at least partially soluble or dissociated in the composition. The ionic strength modifiers can be incorporated into the hair styling compositions, for example, by addition of soluble salts, or by addition of mixtures of acids and bases, or by a combination thereof. It is a necessary aspect of the invention that both anions and cations of the ionic strength modifier system be included in the composition.

Suitable cations for use include, for example, alkali metals, such as lithium, sodium, and potassium, and alkaline-earth metals, such as magnesium, calcium, and strontium. Preferred of the divalent cations is magnesium. Preferred monovalent metal ions are lithium, sodium, and potassium, particularly sodium and potassium. Suitable means of addition to the compositions hereof include, for example, addition as bases, e.g., hydroxides, sodium hydroxide and potassium hydroxide, and such as salts that are soluble in the liquid carrier, e.g. salts of monomeric anions such as those described below.

Other suitable cations include organic ions, such as quaternary ammonium ions and cationic amines, such as ammonium mono-, di-, and triethanolamines, triethylamine, morpholine, aminomethylpropanol (AMP), aminoethylpropanediol, etc. Ammonium and the amines are preferably provided in the forms of salts, such as hydrochloride salts.

Monomeric anions that can be used include halogen ions, such as chloride, fluoride, bromide, and iodide, particularly chloride, sulfate, ethyl sulfate, methyl sulfate, cyclohexyl sulfamate, thiosulfate, toluene sulfonate, xylene sulfonate, citrate, nitrate, bicarbonate, adipate, succinate, saccharinate, benzoate, lactate, borate, isethionate, tartrate, and other monomeric anions that can exist in dissociated form in the hair styling

composition. The anions can be added to the compositions hereof, for example, in the form of acids or salts which are at least partially soluble in the liquid vehicle, e.g., sodium or potassium salts of acetate, citrate, nitrate, chloride, sulfate, etc. Preferably, such salts are entirely soluble in the vehicle.

The use of ionic strength modifiers are especially useful in reduced volatile organic solvent compositions.

The present compositions can also contain various hydrophobic volatile solvents such as cyclomethicone and volatile hydrocarbons such as isododecane and isohexadecane.

The present compositions can contain a wide variety of other optional ingredients, including among them any of the types of ingredients known in the art for use in hair care compositions, especially hair setting compositions such as especially hair spray compositions and hair setting tonics. Generally, such other adjuvants collectively can comprise from about 0.05% to about 5% by weight and preferably from about 0.1% to about 3%, by weight. Such conventional optional adjuvants are well known to those skilled in the art and include, but are not limited to, surfactants (which may be anionic, cationic, amphoteric, or zwitterionic and which include fluorinated surfactants and silicone copolyols), propellants, hair conditioning agents (e.g., silicone fluids, fatty esters, fatty alcohols, long chain hydrocarbons, cationic surfactants, etc.); emollients; lubricants and penetrants such as various lanolin compounds; protein hydrolysates and other protein derivatives; ethylene adducts and polyoxyethylene cholesterol; dyes, tints, bleaches, reducing agents and other colorants; pH adjusting agents; sunscreens; preservatives; thickening agents (e.g. polymeric thickeners, such as xanthan gum); and perfume.

#### Personal Care Products

The compositions of the present invention can be formulated as a wide variety of personal care products. Such products can include shampoos, soaps, hairsprays, lotions, creams, antiperspirants, anti-acne products, nail enamels, lipsticks, foundations, mascaras, and sunscreens.

In preferred embodiments, the compositions of the present invention are formulated as hair spray compositions. These hairspray compositions preferably have removeability values as defined hereinbefore, and may be dispensed as sprayed or atomized products from containers which are pump spray dispensers or aerosol canisters. Such containers are well known to those skilled in the art and are commercially available from a variety of manufacturers, including American National Can Corp. and Continental Can Corp.

When the hair spray compositions are to be dispensed from a pressurized aerosol container, a propellant which consists of one or more of the conventionally-known aerosol propellants can be used to propel the compositions. A suitable propellant for use can be generally any liquifiable gas conventionally used for aerosol containers. Suitable propellants for use are volatile hydrocarbon propellants which can include liquified lower hydrocarbons of 3 to 4 carbon atoms such as propane, butane and isobutane. Other suitable propellants are hydrofluorocarbons such as 1,2-difluoroethane (Hydrofluorocarbon 152A) supplied as Dymel 152A by DuPont. Other examples of propellants are dimethylether, nitrogen, carbon dioxide, nitrous oxide, and atmospheric gas. The hydrocarbons, particularly isobutane, used singly or admixed with other hydrocarbons are preferred.

The aerosol propellant may be mixed with the present hair spray compositions and the amount of propellant to be mixed is governed by normal factors well known in the aerosol art. Generally, for liquifiable propellants, the level of propellant is from about 10% to about 60% by weight of the total composition, preferably from about 15% to about 50% by weight of the total composition.

Alternatively, pressurized aerosol dispensers can be used where the propellant is separated from contact with the hair spray composition such as a two compartment can of the type sold under the tradename SEPRO from American National Can Corp.

Other suitable aerosol dispensers are those characterized by the propellant being compressed air which can be filled into the dispenser by means of a pump or equivalent device prior to use. Such dispensers are described in U.S. Patents 4,077,441, March 7, 1978, Olofsson and 4,850,577, July 25, 1989, TerStegge, both incorporated by reference herein, and in U.S. Serial No. 07/839,648, Gosselin et al., filed February 21, 1992, also incorporated by reference herein. Compressed air aerosol containers suitable for use are also currently marketed by The Procter & Gamble Company under their tradename VIDAL SASSOON AIRSPRAY® hair sprays.

Conventional nonaerosol pump spray dispensers, i.e., atomizers, can also be used.

Other hair styling compositions include tonics and lotions, which are typically dispensed in a conventional bottle or tube, and applied directly to the hair or first dispensed to the hand and then to the hair.

#### Method of Making

The compositions of the present invention, including the preferred hairspray embodiments, can be made using conventional formulation and mixing techniques. The adhesive copolymer and the solvent are mixed to provide a homogeneous mixture. Any

other ingredients are then added and mixed to yield the final composition. If the polymer is neutralized, the neutralizer is preferably added prior to addition of other ingredients. For hair spray products, the composition is packaged in conventional mechanical pump spray devices, or alternatively, in the case of aerosol sprays products, the composition is packaged in conventional aerosol canisters along with an appropriate propellant system.

#### Method of Use

The compositions of the present invention, including the preferred hairspray embodiments of the present invention, are used in conventional ways to provide the benefits of the present invention. These products can be applied to the skin or hair. Typical amounts of products can range from about 0.1 mg/cm<sup>2</sup> to about 25 mg/cm<sup>2</sup> of skin or hair, although a wider range can be used depending upon the exact product application. For hair care products, the methods generally involve application of an effective amount of the product to dry, slightly damp, or wet hair before and/or after the hair is dried and arranged to a desired style. Application of the product is normally effected by spraying or atomizing the product using an appropriate device, e.g. a mechanical pump spray, a pressurized aerosol container, or other appropriate means. The composition is then dried or allowed to dry. By "effective amount" is meant an amount sufficient to provide the hair hold and style benefits desired. In general, from about 0.5g to about 30g of product is applied to the hair, depending upon the particular product formulation, dispenser type, length of hair, and type of hair style.

The following Experimentals and Examples further illustrate embodiments within the scope of the present invention. They are given solely for the purposes of illustration and are not to be construed as limitations of the present invention as many variations of the invention are possible without departing from its spirit and scope.

#### Examples

The following examples further describe and demonstrate embodiments within the scope of the present invention. The examples are given solely for the purpose of illustration and are not to be construed as limitations of the present invention, as many variations thereof are possible without departing from the spirit and scope of the invention. Ingredients are identified by chemical or CTFA name.

#### Examples 1-4: Syntheses of macromonomers and copolymers.

##### Example 1

Synthesis of Vinylphenyl-terminated Poly(n-Propyl methacrylate-co-Methacrylic Acid) Macromonomer

Into a round-bottomed-flask fitted with magnetic stirring and under slight argon pressure (8 psi), is added tetrahydrofuran (1L), trimethylsilylmethacrylate (100g, 0.632 mole), and n-propylmethacrylate (100g, 0.780 mole). The solution is cooled to -80C then initiated with diphenylhexyllithium (0.0275 moles) for chain propagation via anionic polymerization mechanism. After continuous stirring for 0.5 h, vinylbenzoyl chloride (8.33 mL, 0.05 mole) is charged to the solution and continued stirring for 0.5 h. The solution is then warmed to ambient temperature and H<sub>2</sub>O (10mL) is added and stirred for 0.25 hours to deprotect the acid groups. The macromonomer, which has a weight average molecular weight of about 6000, is obtained by precipitating the resulting solution in hexanes, collecting precipitate, and drying under vacuum.

Example 2

Synthesis of Poly(t-butylacrylate-co-2-methoxyethylacrylate-co-acrylic acid)-graft-[poly(Propyl methacrylate-co-Methacrylic Acid)] Copolymer

To a round-bottomed-flask equipped with a reflux condenser, temperature control, mechanical stirring mechanism, and under slight argon pressure (8psi), is added acetone (0.5L), t-butylacrylate (24g), 2-methoxyethylacrylate (38g), acrylic acid (19g), and vinylphenyl-terminated (n-propylmethacrylate-co-methacrylic acid) macromonomer (19g) (from Example 1). Solution is stirred until all components are dissolved, then heated to 60C. Azobisisobutyronitrile (0.7g) is charged to the system. After 10h, solution is cooled and precipitated in water to yield silicone modified graft copolymer.

Example 3

Synthesis of Acryloyl Encapped Polyisobutylene Macromonomer

Prepare a solution of 100 grams (0.024 mol) hydroxyl endcapped polyisobutylene polymer (PIB-OH) having a weight average molecular weight of 4,172 g/mol by conventional living carbocationic polymerization of isobutylene (for example, as described in G. Kaszas, Poly. Bull., 20, 413 (1989). Add a two fold mole excess (4.84 g, 0.048 mol) triethylamine to the solution. Add this solution dropwise to a solution of acryloyl chloride (4.35 g, 0.048 mol) in dry methylene chloride (100 g) at 0 °C. Stir for about 12 hours at room temperature, filter the mixture and evaporate the excess triethylamine and methylene chloride to obtain acryloyl endcapped polyisobutylene macromonomer.



Example 4Synthesis of Poly[(t-butylacrylate-co-2-methoxyethyl acrylate-co-acrylic acid)-graft-[poly(isobutylene)]]

Place 22 parts acrylic acid, 44 parts t-butyl acrylate, 22 parts n-butylacrylate, 12 parts polyisobutylene macromonomer (4172 MW) (from Example 5) in a flask. Add sufficient tetrahydrofuran as the reaction solvent to produce a final monomer concentration of about 20%. Purge the vessel with an inert atmosphere, preferably nitrogen or argon. Add initiator, (2,2'-azobisisobutyronitrile) to a level appropriate for the desired molecular weight. Typically this is in the range of 0.5% to 1.0% by weight relative to the amount of monomer. Heat to 60°C and maintain this temperature for 48 hours while agitating. Terminate the reaction by cooling to room temperature. The polymer is purified by drying off the reaction solvent in an oven. Alternatively, acetone can be used in place of tetrahydrofuran, in which case the polymer is precipitated by adding water and the precipitated polymer is collected and dried.

Examples 5-12

The following examples represent nonaerosol hairspray compositions of the present invention.

	<u>Example No.</u>							
Component (wt%)	5	6	7	8	9	10	11	12
Copolymer 4	4.00	5.00	6.00	4.00	---	---	---	---
Copolymer 2	---	---	---	---	3.00	3.50	2.50	4.00
Isododecane <sup>1</sup>	1.00	---	---	---	---	1.0	2.0	---
Diisobutyl adipate	0.40	---	0.90	0.55	---	---	---	0.40
Sodium hydroxide <sup>2</sup>	0.96	1.20	1.44	---	---	1.20	---	1.35
Potassium hydroxide <sup>3</sup>	--	--	--	1.21	1.00	--	0.70	--
Perfume	0.10	0.10	0.10	0.10	0.10	0.15	0.10	0.15
Water	QS10	QS10	QS10	QS10	QS10	QS10	QS10	QS10
	0	0	0	0	0	0	0	0
Sodium Benzoate	--	--	--	--	0.10	0.10	--	0.10
Ethanol <sup>4</sup>	76.54	71.95	81.56	71.25	79.40	69.26	78.00	55.00

<sup>1</sup> PERMETHYL 99A, from Presperse, Inc., South Plainfield, NJ, USA.

<sup>2</sup> Sodium hydroxide is 30% active.

<sup>3</sup> Potassium hydroxide is 45% active.

<sup>4</sup> SDA 40 (100% ethanol).

### Examples 13-18

The following examples represent aerosol hairspray compositions of the present invention.

Component (wt%)	<u>Example No.</u>					
	13	14	15	16	17	18
Copolymer 2	5.00	4.00	3.50	---	---	---
Copolymer 4	---	---	---	4.00	3.00	4.00
Isododecane <sup>1</sup>	0.50	---	---	--	--	0.50
Triethyl citrate <sup>2</sup>	--	--	0.21	--	--	--
Diisobutyl adipate	0.70	0.45	--	0.40	0.25	0.35
Propylene glycol	--	--	0.30	--	---	---
Sodium hydroxide <sup>3</sup>	1.00	--	--	--	1.0	---
Potassium hydroxide <sup>4</sup>	--	0.94	1.20	1.04	---	1.20
Perfume	0.10	0.10	0.10	0.10	0.10	0.10
Water	QS100	QS100	QS100	QS100	QS100	QS100
Sodium Benzoate	0.10	0.10	--	0.10	0.20	--
Ethanol <sup>5</sup>	56.69	57.42	72.0	50.0	30.00	54.5
Propellant - Isobutane	--	--	7.02	15.00	10.00	--
Propellant - n-butane	10.00	---	--	--	--	--
Propellant - Dimethyl ether <sup>6</sup>	10.00	---	--	15.00	15.00	--
Propellant - Hydrofluorocarbon 152a <sup>7</sup>	--	25	15.98	--	--	32.32

<sup>1</sup> PERMETHYL 99A, from Presperse, Inc., South Plainfield, NJ, USA.

<sup>2</sup> CITROFLEX-2, from Morflex, Inc., Greensboro, NC, USA.

<sup>3</sup> Sodium hydroxide is 30% active.

<sup>4</sup> Potassium hydroxide is 45% active.

<sup>5</sup> SDA 40 (100% ethanol).

<sup>6</sup> DYMEL - A, from Dupont.

<sup>7</sup> DYMEL-152a, from Dupont.

The compositions are prepared as described above, by first mixing the polymer with the ethanol, neutralizing the polymer with sodium or potassium hydroxide, then

adding sequentially (as applicable) with mixing, isododecane, plasticizer, perfume, and water. If sodium benzoate is used, it is added after water addition. Most preferably a premix of water and sodium benzoate is made and then added after the main water addition. Propellants for aerosol compositions are charged to conventional aerosol containers after the remainder of the prepared composition has been added.

The hair spray embodiments of the present invention described in Examples 5-18 have high removeability from hair, and when evaluated by the removeability methodology described herein, provide a hair stiffness value of less than 2.0 and a hair flaking value of less than 2.0.

While particular embodiments of the subject invention have been described, it will be obvious to those skilled in the art that various changes and modifications to the subject invention can be made without departing from the spirit and scope of the invention. It is intended to cover, in the appended claims, all such modifications that are within the scope of the subject invention.

#### EXAMPLE 19

The following is a hair conditioner composition representative of the present invention.

<u>Ingredients</u>	<u>Weight %</u>
Water	Q.S. to 100%
Perfume	0.10
Stearalkonium Chloride	0.87
Methylchloroisothiazolinone Methylisothiazolinone	0.03
Sodium Hydroxide Solution (30% by weight)	0.70
Polymer 2	3.00
Ethanol	20.0

This product is prepared by dispersing the copolymer 3 in ethanol then adding the remaining ingredients and stirring for about 30 minutes.

#### EXAMPLE 20

The following is a hair styling gel composition representative of the present invention.

<u>Ingredients</u>	<u>Weight %</u>
Copolymer 4	2.50

Water	QS 100%
Carbomer 940	0.50
Sodium Hydroxide Solution (30% by weight)	0.80
Panthenol	0.05
Polysorbate 80	0.20
Perfume	0.20

This product is prepared by dispersing the copolymer # 4 and carbomer 940 in water and adding the sodium hydroxide. The mixture is stirred for approximately one half hour and the remaining components are added.

#### EXAMPLE 21

The following is a spray-on gel hair composition representative of the present invention.

<u>Ingredients</u>	<u>Weight %</u>
Water	Q.S. to 100 %
Ethanol	15.00
Panthenol	0.05
Potassium Hydroxide Solution (45% by weight)	0.50
Perfume	0.20
Copolymer # 2	2.00

This product is prepared by dissolving the copolymer # 2 ethanol and then adding the water and potassium hydroxide solution to facilitate the incorporation of the copolymer into the solvent. The mixture is stirred for one half hour and the other components are mixed in.

#### EXAMPLE 22

The following is a hair styling mousse composition representative of the present invention.

<u>Ingredients</u>	<u>Weight %</u>
Water	Q.S. to 100 %
Lauramine Oxide	0.20
Panthenol	0.05
Perfume	0.05
Copolymer #4	3.00
Sodium Hydroxide Solution (30% by weight)	1.00
Isobutane	7.00

This product is prepared by dissolving the copolymer #2 in water and adding the sodium hydroxide solution with mixing for one half hour. The other components (except isobutane) are added and mixed for an additional 10 minutes. Aluminum aerosol cans are then filled with 93 parts of this batch, affixed with a valve which is crimped into position, and lastly pressure filled with 7 parts Isobutane. This composition is useful for application to the hair to provide conditioning, styling and hold.

### EXAMPLE 23

#### Sunscreen Composition

<u>Ingredients</u>	<u>Weight %</u>
Water	QS100
Carbomer 1342 <sup>[1]</sup>	0.16
Octyl Methoxycinnamate	0.50
Dimethicone copolyol	0.10
Tocopheryl Acetate	0.10
Sodium Hydroxide (30% sol. by weight)	1.50
Ethanol	40.00
Copolymer #4	4.00

[1] Available as Carbopol® 1342 from B.F. Goodrich.

The water, ethanol, sodium hydroxide solution and polymer 4 are mixed for one half hour. The remaining ingredients are added and mixed for an additional half hour.

### EXAMPLE 24

The following is an anti-acne composition representative of the present invention.

<u>Ingredients</u>	<u>Weight %</u>
Copolymer # 2	2.00
Water	Q.S. to 100 %
Ethanol (SDA 40)	40.00
Carbomer 940	0.75
Sodium Hydroxide Solution (30% by weight)	0.90
Salicylic Acid	2.00

This product is prepared by mixing the water, ethanol, copolymer 2, and carbomer together for about 10 minutes. The remaining ingredients are added and the mixture is stirred for an additional 30 minutes. This composition is useful for application to the skin to provide improved water resistance and is useful in the treatment of acne.

EXAMPLE 25

The following is a nail polish clear coat composition representative of the present invention.

<u>Ingredients</u>	<u>Weight %</u>
Copolymer # 4	15.00
Ethanol	42.00
Acetone	40.00
NaOH soln., 30%	3.00

This product is prepared by mixing all the ingredients until dispersed.

EXAMPLE 26

The following is a facial wrinkle remover composition representative of the present invention.

<u>Ingredients</u>	<u>Weight %</u>
Copolymer # 4	6.00
NaOH soln., 30%	2.10
DRO water	q.s.

This product is prepared by mixing all the ingredients until dispersed.

EXAMPLE 27

The following is a styling lotion composition representative of the present invention.

<u>Ingredients</u>	<u>Weight %</u>
Copolymer # 2	4.00
Natrosol 250HH <sup>1</sup>	0.50
NaOH soln., 30%	1.35
Kathon CG	0.03
Ethanol	8.00
DRO water	q.s.

<sup>1</sup> Natrosol 250HH-Hydroxyethylcellulose offered by Aqualon.

The copolymer is first dissolved in the ethanol and then added to a premix composed of the remaining ingredients and mixed until well dispersed.

EXAMPLE 28

The following is an aftershave splash composition representative of the present invention.

<u>Ingredients</u>	<u>Weight %</u>
Copolymer # 2	2.00
NaOH soln., 30%	0.60
Ethanol	50.00
Perfume	0.20
Menthol	0.20
DRO water	q.s.

This product is prepared by mixing all the ingredients until dispersed.

**What is claimed is:**

1. A personal care composition, comprising:
  - (a) an adhesive copolymer having a weight average molecular weight from 10,000 to 5,000,000, and
  - (b) a solvent for said copolymer selected from the group consisting of water, ethanol, n-propanol, isopropanol, acetone, propylene glycol, and mixtures thereof,wherein said composition, when dried, has a cohesive strength of greater than  $0.5 \text{ kgf/mm}^2$ , a total energy absorption per unit volume of greater than  $0.55 \text{ kgfmm/mm}^3$ , and an impact strength of greater than 7000 ergs.
2. A composition according to Claim 1 wherein the composition is a hair spray composition which provides a hair stiffness value of from 0 to 2.0 and a hair flaking value of from 0 to 2.0.
3. A composition according to either of Claims 1 or 2 wherein said copolymer is soluble or dispersible in said solvent at a concentration of at least  $0.1 \text{ mg/mL}$  at  $73^\circ\text{F}$ .
4. A composition according to any one of the preceding claims wherein said composition, when dried, has a cohesive strength of greater than  $0.7 \text{ kgf/mm}^2$ , a total energy absorption of greater than  $1.10 \text{ kgfmm/mm}^3$ , and an impact strength of greater than 50,000 ergs.
5. A composition according to any one of the preceding claims wherein said copolymer is formed from the random copolymerization of the following relative weight percentages of vinyl monomer units and polysiloxane-containing macromonomer units:
  - a. from 50% to 98%, by weight of said copolymer, of vinyl monomer units, and
  - b. from 2% to 50%, by weight of said copolymer, of macromonomer units, wherein said polysiloxane-containing macromonomer units have a weight average molecular weight from 1,000 to 50,000.
6. A composition according to Claim 5 wherein said vinyl monomer units are selected from the group consisting of acrylic acid, methacrylic acid, N,N-dimethyl acrylamide, dimethylaminoethyl methacrylate, quaternized dimethylaminoethyl methacrylate, vinyl pyrrolidone, acrylic or methacrylic acid esters of  $\text{C}_{1-18}$  alcohols, styrene, alpha-methylstyrene, t-butylstyrene, vinyl acetate, vinyl propionate, vinyl chloride, vinylidene chloride, vinyl toluene, butadiene, cyclohexadiene, ethylene, propylene n-butyl methacrylate, isobutyl methacrylate, t-butyl acrylate, t-butyl methacrylate, 2-ethylhexyl methacrylate, methyl methacrylate, salts of any acids and amines listed above, and combinations thereof.



7. A composition according to any one of preceding Claims 1, 2, 3 or 4 wherein said copolymer is a block copolymer.
8. A composition according to any one of preceding Claims 1, 2, 3 or 4 wherein said copolymer is a graft copolymer.
9. A method of styling hair comprising the step of applying to the hair an effective amount of a composition according to any one of the preceding claims.

1/1

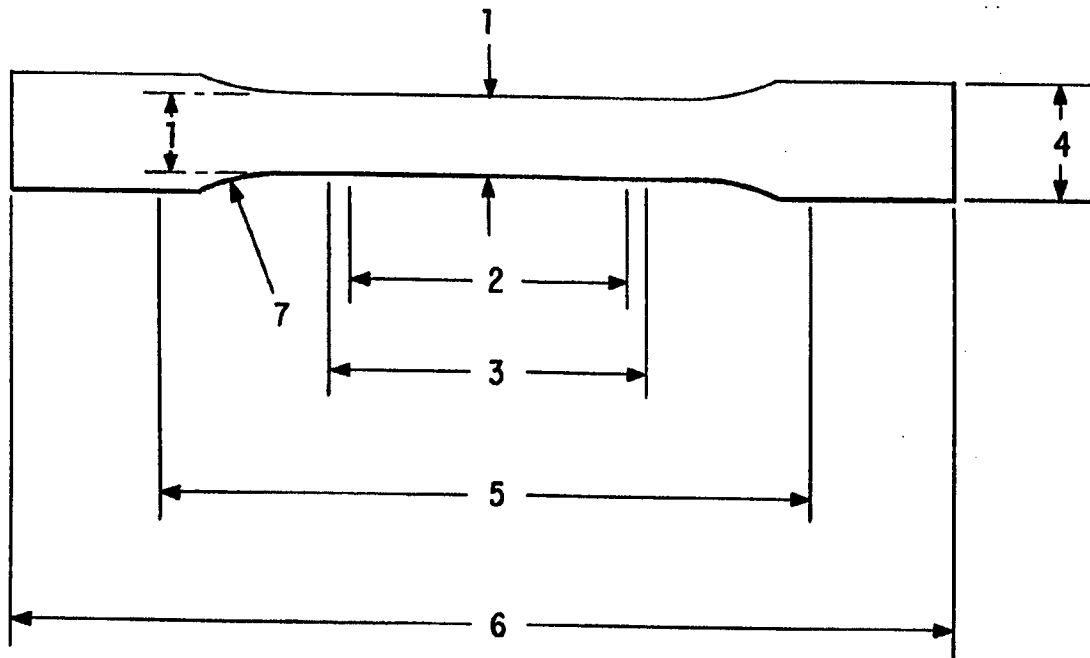


FIG. 1

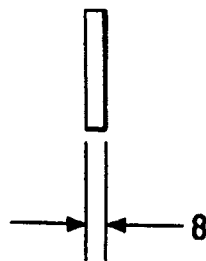


FIG. 2

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 98/08347

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 A61K7/06

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 766 957 A (WAKO PURE CHEM IND LTD ;MANDOM CORP (JP)) 9 April 1997 see abstract; examples ----	1,2,5-7, 9
T	US 5 653 968 A (CARBALLADA JOSE ANTONIO ET AL) 5 August 1997 see column 2, line 12 - line 49 see column 4, line 44 - column 5, line 28 see column 7, line 18 - line 67 ----	1,2,5,6, 8,9
A	WO 96 32918 A (PROCTER & GAMBLE) 24 October 1996 ----	
A	EP 0 408 311 A (MITSUBISHI PETROCHEMICAL CO) 16 January 1991 cited in the application -----	



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

### \* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

7 August 1998

Date of mailing of the international search report

17/08/1998

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

McConnell, C

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 98/08347

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0766957 A	09-04-1997	CN 1158720 A JP 9157339 A	10-09-1997 17-06-1997
US 5653968 A	05-08-1997	WO 9734573 A	25-09-1997
WO 9632918 A	24-10-1996	AU 5528396 A EP 0822801 A	07-11-1996 11-02-1998
EP 0408311 A	16-01-1991	DE 69028742 D JP 3128909 A US 5480634 A US 5166276 A	07-11-1996 31-05-1991 02-01-1996 24-11-1992



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup> :</b> <b>A61K 7/48, 7/06</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 98/48776</b> <b>(43) International Publication Date:</b> 5 November 1998 (05.11.98)
<b>(21) International Application Number:</b> PCT/US98/08285 <b>(22) International Filing Date:</b> 24 April 1998 (24.04.98)  <b>(30) Priority Data:</b> 08/846,058      25 April 1997 (25.04.97)      US  <b>(71) Applicant:</b> THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US).  <b>(72) Inventors:</b> MIDHA, Sanjeev; Apartment 2D, 9274 Deercross Parkway, Cincinnati, OH 45236 (US). MCDONOUGH, Sean, Patrick; Apartment 8, 1056 Delta Avenue, Cincinnati, OH 45208 (US).  <b>(74) Agents:</b> REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217 (US).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the</i> <i>claims and to be republished in the event of the receipt of</i> <i>amendments.</i>
<b>(54) Title:</b> PERSONAL CARE COMPOSITIONS CONTAINING LINEAR TOUGHENED SILICONE GRAFTED POLYMERS		
<b>(57) Abstract</b> <p>A personal care composition comprising: (a) a silicone grafted adhesive polymer, said polymer being characterized by an organic polymeric backbone wherein said backbone comprises: (i) at least one monomer wherein when said monomer is polymerized as a homopolymer having a Tg of from about -120 °C to about 25 °C and (ii) at least one monomer wherein when said monomer is polymerized as a homopolymer having a Tg of from above about 25 °C to about 250 °C wherein said silicone grafted adhesive polymer has silicone macromers grafted to said backbone and wherein the number average molecular weight of said silicone macromers is greater than about 1000; and (b) a personal care carrier.</p>		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Licchtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

## PERSONAL CARE COMPOSITIONS CONTAINING LINEAR TOUGHENED SILICONE GRAFTED POLYMERS

### TECHNICAL FIELD

The present invention relates to personal care compositions, such as haircare, cosmetic and nail compositions containing linear toughened silicone grafted polymers.

### BACKGROUND OF THE INVENTION

Cosmetic compositions such as lotions, creams, emulsions, packs, make-up (e.g., foundations, lipsticks, eye shadows and the like) and hair compositions are used to improve one's outward appearance. Many personal care products use contain various resins, gums, and adhesive polymers. The polymers are used for a variety of purposes including thickening, feel properties, film-forming ability, active deposition, active penetration, hair holding, etc. Consequently there is constantly a search for developing polymers having improved properties for use in personal care product. Many of these compositions require the use of adhesive silicone grafted polymers. For example, the desire to have the hair retain a particular shape is widely held. The most common methodology for accomplishing this is the application of a styling composition to dampened hair, after shampooing and/or conditioning, or to dry, styled hair. These compositions provide temporary setting benefits and they can be removed by water or by shampooing. The materials used in the compositions to provide the setting benefits have generally been resins and have been applied in the form of mousses, gels, lotions or sprays.

Many people desire a high level of style retention, or hold, from a hair spray composition. In typical hair sprays, hold is achieved by the use of resins, such as AMPHOMER<sup>R</sup>, supplied by National Starch and Chemical Company, and GANTREZ<sup>R</sup> SP 225, supplied by GAF. In general, as hair hold for hair spray compositions is increased, the tactile

feel of the hair becomes stiffer and hence, less desirable. It is desirable to provide hair spray products which could provide an improved combination of hair hold and hair feel characteristics.

Recently, it has become known to utilize silicone grafted organic backbone polymers in various personal care compositions including their use as hair setting agents in hairspray compositions and other hair styling compositions, e.g. hair tonics, lotions, rinses, mousses, etc. Silicone grafted polymers can be used to make personal care compositions with improved feel, e.g., in the case of hair sprays, increased softness relative to conventional polymeric hair setting agents.

However, it remains desirable to improve the performance of these silicone grafted polymers. It is an object of this invention to provide personal care compositions containing linear toughened silicone graft copolymers.

It is a further object of this invention to provide personal care compositions containing resins that have improved adhesive and cohesive properties thereby providing improved durability benefits (e.g., style benefits).

These and other benefits as may be apparent from the description below can be obtained by the present invention.

The present compositions can comprise, consist of, or consist essentially of any of the required or optional ingredients and/or limitations described herein.

All percentages and ratios are calculated on a weight basis unless otherwise indicated. All percentages are calculated based upon the total composition unless otherwise indicated.

All ingredient levels refer to the active level of that ingredient, and are exclusive of solvents, by-products, or other impurities that may be present in commercially available sources, unless otherwise indicated.



## SUMMARY OF THE INVENTION

The present invention relates to a personal care composition comprising:

- (a) a silicone grafted adhesive polymer, said polymer being characterized by an organic polymeric backbone wherein said backbone comprises
  - (i) at least one monomer wherein when said monomer is polymerized as a homopolymer having a Tg of from about -120° C to about 25° C and
  - (ii) at least one monomer wherein when said monomer is polymerized as a homopolymer having a Tg of from above about 25° C to about 250° Cwherein said silicone grafted adhesive polymer has silicone macromers grafted to said backbone and wherein the number average molecular weight of said silicone macromers is greater than about 1000; and
- (b) a personal care carrier.

## DETAILED DESCRIPTION OF THE INVENTION

The essential components of the present invention are described below. Also included is a nonexclusive description of various optional and preferred components useful in embodiments of the present invention.

Silicone Grafted Adhesive Polymer

The compositions according to the invention comprise, as an essential component, a silicone grafted adhesive polymer, said polymer being characterized by an organic polymeric backbone wherein said backbone comprises:

- (a) at least one monomer wherein when said monomer is polymerized as a homopolymer having a Tg of from about -120° C to about 25° C and

(b) at least one monomer wherein when said monomer is polymerized as a homopolymer having a Tg of from above about 25° C to about 250° C

wherein said silicone grafted adhesive polymer has silicone macromers grafted to said backbone and wherein the number average molecular weight of said silicone macromers is greater than about 1000. This silicone containing hair styling polymer is preferably colloidally dispersed or solubilized in any applicable carrier.

The compositions hereof will generally comprise from about 0.1% to about 99%, preferably from 0.5% to about 50%, more preferably from about 1% to about 10%, by weight of the composition, of the silicone grafted polymer. It is not intended to exclude the use of higher or lower levels of the polymers, as long as an effective amount is used to provide adhesive or film-forming properties to the composition and the composition can be formulated and effectively applied for its intended purpose. By adhesive polymer what is meant is that when applied as a solution to a surface and dried, the polymer forms a film or a weld. Such a film will have adhesive and cohesive strength, as is understood by those skilled in the art.

The silicone grafted polymers are characterized by polysiloxane moieties covalently bonded to and pendant from a polymeric carbon-based backbone.

The backbone will preferably be a carbon chain derived from polymerization of ethylenically unsaturated monomers. The backbone comprises (a) at least one monomer wherein when said monomer is polymerized as a homopolymer having a Tg of from about -120° C to about 25° C and (b) at least one monomer wherein when said monomer is polymerized as a homopolymer having a Tg of from above about 25° C to about 250° C. The polysiloxane moieties can be substituted on the polymer or can be made by co-polymerization of polysiloxane-containing polymerizable monomers (e.g. ethylenically unsaturated monomers, ethers,

and/or epoxides) with non-polysiloxane-containing polymerizable monomers.

The polysiloxane-grafted polymer should have a weight average molecular weight of at least about 20,000. There is no upper limit for molecular weight except that which limits applicability of the invention for practical reasons, such as processing, aesthetic characteristics, formulateability, etc. In general, the weight average molecular weight will be less than about 10,000,000, more generally less than about 5,000,000, and typically less than about 3,000,000. Preferably, the weight average molecular weight will be between about 50,000 and about 2,000,000, more preferably between about 75,000 and about 1,000,000, most preferably between about 100,000 and about 750,000.

Preferably, the adhesive hereof when dried to form a film have a Tg of at least about -20°C, more preferably at least about -5°C, so that they are not unduly sticky, or "tacky" to the touch. As used herein, the abbreviation "Tg" refers to the glass transition temperature of the backbone of the polymer, if such a transition exists for a given polymer. Preferably, the Tg is above about -20°C, more preferably above about -5°C. Preferably the adhesive polymer of the present invention has a Tg below about 60°C, more preferably below about 50°C and most preferably below about 40°C.

The silicone grafted polymers for the compositions of the present invention comprise "silicone-containing" (or "polysiloxane-containing") monomers, which form the silicone macromer pendant from the backbone, and non-silicone-containing monomers, which form the organic backbone of the polymer.

When used in a composition, such as a personal care composition for application to the hair or skin, the non-polysiloxane portion should permit the polymer to deposit on the intended surface, such as hair or skin.

The polysiloxane macromer should have a weight average molecular weight of at least about 1000, preferably from about 1,000 to about 50,000, more preferably from about 5,000 to about 50,000, most preferably about

8,000 to about 25,000. Organic backbones contemplated include those that are derived from polymerizable, ethylenically unsaturated monomers, including vinyl monomers, and other condensation monomers (e.g., those that polymerize to form polyamides and polyesters), ring-opening monomers (e.g., ethyl oxazoline and caprolactone), etc.

The preferred silicone grafted polymers are comprised of monomer units derived from: at least one free radically polymerizable ethylenically unsaturated monomer or monomers and at least one free radically polymerizable polysiloxane-containing ethylenically unsaturated monomer or monomers.

#### Vinyl Monomer Units

The silicone copolymers of the present invention comprise from about 50% to about 98%, preferably from about 60% to about 95%, and more preferably from about 70% to about 90% by weight of the vinyl monomer units.

The vinyl monomer unit is selected from copolymerizable monomers, preferably ethylenically unsaturated monomers. The vinyl monomers are selected to meet the requirements of the copolymer. By "copolymerizable", as used herein, is meant that the vinyl monomer can be reacted with or polymerized with the polysiloxane macromonomers in a polymerization reaction using one or more conventional synthetic techniques, such as ionic, emulsion, dispersion, Ziegler-Natta, free radical, group transfer or step growth polymerization. In the present invention, monomers and macromonomers that are copolymerizable using conventional free radical initiated techniques are preferred. The term "ethylenically unsaturated" is used herein to mean a material that contains at least one polymerizable carbon-carbon double bond, which can be mono-, di-, tri- or tetra-substituted.

The monomer units can be derived from hydrophilic monomers (typically polar monomers), or mixtures of such hydrophilic monomers with hydrophobic monomers (typically low polarity monomers), provided that the

solubility characteristics of the overall copolymer is achieved. As used herein, "hydrophilic monomers" means monomers which form homopolymers which are substantially water soluble; "hydrophobic monomers" means monomers which form substantially water insoluble homopolymers.

Nonlimiting classes of monomers useful herein include monomers selected from the group consisting of unsaturated alcohols, unsaturated monocarboxylic acids, unsaturated dicarboxylic acids, unsaturated anhydrides, alcohol esters of unsaturated monocarboxylic acids, alcohol esters of unsaturated dicarboxylic acids, alcohol esters of unsaturated anhydrides, alkoxyated esters of unsaturated monocarboxylic acids, alkoxyated esters of unsaturated dicarboxylic acids, alkoxyated esters of unsaturated anhydrides, aminoalkyl esters of unsaturated monocarboxylic acids, aminoalkyl esters of unsaturated dicarboxylic acids, aminoalkyl esters of unsaturated anhydrides, amides of unsaturated monocarboxylic acids, amides of unsaturated dicarboxylic acids, amides of unsaturated anhydrides, salts of unsaturated monocarboxylic acids, salts of unsaturated dicarboxylic acids, salts of unsaturated anhydrides, unsaturated hydrocarbons, unsaturated heterocycles, and mixtures thereof.

Representative examples of such monomers include acrylic acid, methacrylic acid, N,N-dimethylacrylamide, dimethylaminoethyl methacrylate, quaternized dimethylaminoethyl methacrylate, methacrylamide, N-t-butyl acrylamide, maleic acid, maleic anhydride and its half esters, crotonic acid, itaconic acid, acrylamide, acrylate alcohols, hydroxyethyl methacrylate, diallyldimethyl ammonium chloride, vinyl pyrrolidone, vinyl ethers (such as methyl vinyl ether), maleimides, vinyl pyridine, vinyl imidazole, other polar vinyl heterocyclics, styrene sulfonate, allyl alcohol, vinyl alcohol (such as that produced by the hydrolysis of vinyl acetate after polymerization), vinyl caprolactam, methacrylic acid esters of C<sub>1</sub>-C<sub>18</sub> alcohols, such as methanol, ethanol, methoxy ethanol, 1-propanol, 2-propanol, 1-butanol, 2-methyl-1-propanol, 1-pentanol, 2-pentanol, 3-pentanol, 2-methyl-1-butanol, 1-methyl-

1-butanol, 3-methyl-1-butanol, 1-methyl-1-pentanol, 2-methyl-1-pentanol, 3-methyl-1-pentanol, t-butanol(2-methyl-2-propanol), cyclohexanol, neodecanol, 2-ethyl-1-butanol, 3-heptanol, benzyl alcohol, 2-octanol, 6-methyl-1-heptanol, 2-ethyl-1-hexanol, 3,5-dimethyl-1-hexanol, 3,5,5-trimethyl-1-hexanol, 1-decanol, 1-dodecanol, 1-hexadecanol, 1-octadecanol, and the like, the alcohols having from about 1-18 carbon atoms with the number of carbon atoms preferably being from about 1-12; dicyclopentenyl acrylate; 4-biphenyl acrylate; pentachlorophenyl acrylate; 3,5-dimethyladamantyl acrylate; 3,5-dimethyladamantyl methacrylate; 4-methoxycarbonylphenyl methacrylate; trimethylsilyl methacrylate; styrene; alkyl substituted styrenes including alpha-methylstyrene and t-butylstyrene; vinyl esters, including vinyl acetate, vinyl neononanoate, vinyl pivalate and vinyl propionate; vinyl chloride; vinylidene chloride; vinyl toluene; alkyl vinyl ethers, including isobutyl vinyl ether and s-butyl vinyl ether; butadiene; cyclohexadiene; bicycloheptadiene; 2,3-dicarboxylmethyl-1,6-hexadiene; ethylene; propylene; indene; norbornylene;  $\beta$ -pinene;  $\alpha$ -pinene; salts of acids and amines listed above, and combinations thereof. The quaternized monomers can be quaternized either before or after the copolymerization with other monomers of the graft copolymer.

Preferred monomers include acrylic acid, methacrylic acid, N,N-dimethyl acrylamide, dimethylaminoethyl methacrylate, quaternized dimethylaminoethyl methacrylate, vinyl pyrrolidone, acrylic or methacrylic acid esters of C<sub>1</sub>-C<sub>18</sub> alcohols, styrene, alpha-methylstyrene, t-butylstyrene, vinyl acetate, vinyl propionate, 2-methoxyethyl acrylate, 2-ethoxyethyl acrylate, n-butyl methacrylate, isobutyl methacrylate, t-butyl acrylate, t-butyl methacrylate, 2-ethylhexyl methacrylate, methyl methacrylate, salts of any acids and amines listed above, and mixtures thereof.

From the above descriptions, esters of acrylic and methacrylic acid that form low T<sub>g</sub> homopolymers include, for example, 3-methoxybutyl acrylate, 2-methoxyethyl acrylate, 2-phenoxyethyl ester, 2-hydroxyethyl

ester, 4-hydroxybutyl acrylate, 2-ethoxyethoxyethyl acrylate, 2-ethoxyethyl acrylate, n-butyl acrylate, dodecyl acrylate, 2-ethylhexyl acrylate, 2-ethylbutyl acrylate, n-ethyl acrylate, n-heptyl acrylate, n-hexyl acrylate, iso-butyl acrylate, iso-decyl acrylate, iso-propyl acrylate, 3-methylbutyl acrylate, 2-methylpentyl acrylate, nonyl acrylate, octyl acrylate, 2-ethylhexyl methacrylate, n-pentyl methacrylate; Acrylamide monomers including N-dodecylacrylamide, N-octadecylacrylamide; Vinyl monomers including sec-butyl vinyl ether, butyl vinyl ether, vinyl propionate, vinyl butyrate, decylvinyl ether, methyl vinyl ether and Styrene monomers including 4-decylstyrene. Other monomers that form low Tg homopolymers include isobutylene, 1-butene, 5-methyl-1-hexene, olefinic monomers that could be hydrogenated post polymerization (after formation of copolymers), for example, isoprene, 1,2-butadiene, 1,4-butadiene.

Preferred monomers which form low Tg homopolymers include 3-methoxybutyl acrylate, 2-methoxyethyl acrylate, n-butyl acrylate, dodecyl acrylate, 2-ethylhexyl acrylate, 2-ethylbutyl acrylate, ethyl acrylate, n-heptyl acrylate, n-hexyl acrylate, iso-butyl acrylate, iso-decyl acrylate, iso-propyl acrylate, 3-methylbutyl acrylate, 2-methylpentyl acrylate, nonyl acrylate, octyl acrylate, 2-ethylhexyl methacrylate, n-pentyl methacrylate, N-octadecylacrylamide.

Most Preferred monomers which form low Tg homopolymers include 2-methoxyethyl acrylate, n-butyl acrylate, ethyl acrylate. These low Tg monomers preferably have Tg of from about -70°C to about 25°C, more preferably from about -60°C to about 0°C and most preferably from about -60°C to about -20°C.

From the above descriptions, acrylic and methacrylic acids that form high Tg homopolymers include, for example, sec-butyl methacrylate, t-butyl acrylate, methyl methacrylate, isopropyl methacrylate, 2-t-butylaminoethyl methacrylate, dimethyl aminoethyl methacrylate, quaternized dimethyl aminoethyl methacrylate, 4-biphenyl acrylate, pentachlorophenyl acrylate, 3,5-dimethyladamantyl acrylate, 3,5-dimethyladamantyl methacrylate,

isobornyl acrylate, trimethylsilyl methacrylate, trimethylsilyl acrylate (silyl esters could be hydrolysed to form acrylic or methacrylic acids), acrylic acid, methacrylic acid, salts of acrylic and methacrylic acids; Acrylamide & methacrylamide monomers including N-butylacrylamide, acrylamide, N-isopropylacrylamide, N-t-butylmethacrylamide; Vinyl monomers including: 2-vinylpyridine, 4-vinylpyridine, vinyl acetate, vinyl chloride, N-vinylcaprolactam, N-vinyl pyrrolidone, cyclohexyl vinyl ether, vinyl alcohol, vinyl imidazole; Styrene monomers including: styrene, 4-t-butylstyrene, 2-methoxystyrene, 4-acetylstyrene, styrene sulfonate. Other monomers that form high Tg homopolymers include: diallyldimethylammonium chloride, maleimides, crotonic acid, itaconic acid, maleic anhydrides, allyl alcohol,  $\alpha$ -pinene,  $\beta$ -pinene, tert-butyl styrene,  $\alpha$ -methyl styrene, indene, norbornene, norbornylene.

Preferred monomers which form high Tg homopolymers include: t-butyl methacrylate, t-butyl acrylate, methyl methacrylate, dimethyl aminoethyl methacrylate, isopropyl methacrylate, trimethylsilyl methacrylate, trimethylsilyl acrylate, acrylic acid, methacrylic acid, salts of acrylic and methacrylic acids, tert-butyl styrene,  $\alpha$ -methyl styrene, 2-vinylpyridine, 4-vinylpyridine, N-isopropylacrylamide, N-t-butylmethacrylamide.

Most Preferred monomers which form high Tg homopolymers include: t-butyl methacrylate, t-butyl acrylate, methyl methacrylate, acrylic acid, methacrylic acid, salts of acrylic and methacrylic acids, tert-butyl styrene. These high Tg monomers preferably have Tg of from above about 25° C to about 250° C, more preferably from about 30° C to about 200° C, even more preferably from about 35° C to about 150° C, and most preferably from about 40° C to about 130° C.

#### Polysiloxane Macromonomer Units

The copolymers of the present invention comprise from about 2% to about 50%, preferably from about 5% to about 40%, and more preferably from about 10% to about 30%, by weight of the copolymer of polysiloxane macromonomer units.



The polysiloxane macromonomer units are copolymerizable with the vinyl monomers, said macromonomers preferably having a vinyl moiety. Either a single type of macromonomer unit or combinations of two or more macromonomer units can be utilized herein. The macromonomers are selected to meet the requirements of the copolymer. By "copolymerizable", as used herein, is meant that the macromonomers can be reacted with or polymerized with the vinyl monomers in a polymerization reaction using one or more conventional synthetic techniques, as described above.

The polysiloxane macromonomers that are useful herein contain a polymeric portion and a copolymerizable moiety which is preferably an ethylenically unsaturated moiety. Typically, the preferred macromonomers are those that are endcapped with the vinyl moiety. By "endcapped" as used herein is meant that the vinyl moiety is at or near a terminal position of the macromonomer.

The macromonomers can be synthesized utilizing a variety of standard synthetic procedures familiar to the polymer chemist of ordinary skill in the art. Furthermore, these macromonomers can be synthesized starting from commercially available polymers. Typically, the weight average molecular weight of the macromonomer is from about 1000 to about 50,000.

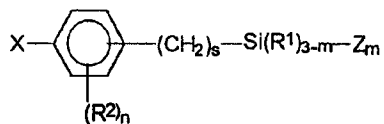
Polysiloxane macromonomers are exemplified by the general formula:



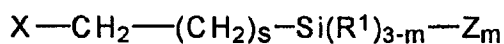
wherein X is a vinyl group copolymerizable with the vinyl monomer units; Y is a divalent linking group; each R is independently selected from the group consisting of hydrogen, hydroxyl, C1-C6 alkyl, C1-C6 alkoxy, C2-C6 alkylamino, phenyl, C1-C6 alkyl or alkoxy-substituted phenyl; Z is a monovalent siloxane polymeric moiety having a number average molecular weight of at least about 1000, is essentially unreactive under copolymerization conditions, and is pendant from the vinyl polymeric backbone described above; n is 0 or 1; and m is an integer from 1 to 3. The polysiloxane macromonomer has a weight average molecular weight from

about 1000 to about 50,000, preferably from about 5,000 to about 30,000, more preferably from about 8,000 to about 25,000.

Preferably, the polysiloxane macromonomer has a formula selected from the following formulas:



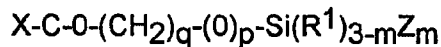
or



or

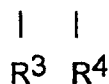
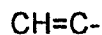
0

°

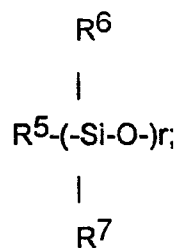


In these structures s is an integer from 0 to 6; preferably 0, 1, or 2; more preferably 0 or 1; m is an integer from 1 to 3, preferably 1; p is 0 or 1; q is an integer from 2 to 6; each R<sup>1</sup> is independently selected from the group consisting of hydrogen, hydroxyl, C1-C6 alkyl, C1-C6 alkoxy, C2-C6 alkylamino, phenyl, C1-C6 alkyl or alkoxy-substituted phenyl, preferably C1-C6 alkyl, or C1-C6 alkyl or alkoxy-substituted phenyl, more preferably C1-C6 alkyl, even more preferably methyl, R<sup>2</sup> is selected from the group consisting of C1-C6 alkyl or C1-C6 alkyl substituted phenyl, preferably methyl.

n is an integer from 0 to 4, preferably 0 or 1, more preferably 0; X is



wherein R<sup>3</sup> is hydrogen or -COOH, preferably R<sup>3</sup> is hydrogen; R<sup>4</sup> is hydrogen, methyl or -CH<sub>2</sub>COOH, preferably R<sup>4</sup> is methyl; Z is



wherein  $R^5$ ,  $R^6$ , and  $R^7$ , are independently selected from hydrogen, hydroxyl, C1-C6 alkyl, C1-C6 alkoxy, C2-C6 alkylamino, phenyl, C1-C6 alkyl or alkoxy-substituted phenyl, hydrogen or hydroxyl, preferably  $R^5$ ,  $R^6$ , and  $R^7$  are C1-C6 alkyls; more preferably methyl; and  $r$  is an integer of from about 14 to about 700, preferably about 60 to about 400, and more preferably about 100 to about 350.

Exemplary silicone grafted polymers for use in the present invention include the following, where the composition is given as weight part of monomer used in the synthesis:

- (i) poly(t-butyl acrylate-co-n-butyl acrylate-co-acrylic acid-co-methacrylic acid)-graft-poly(dimethylsiloxane)  
 MWt of copolymer: 210,000  
 Composition: t-butyl acrylate (36%), n-butyl acrylate (27%), acrylic acid (12%), methacrylic acid (10%), poly(dimethylsiloxane) (15%)  
 MWt of poly(dimethylsiloxane): 10,000
- (ii) poly(t-butyl acrylate-co-ethyl acrylate-co-acrylic acid)-graft-poly(dimethylsiloxane)  
 MWt of copolymer: 100,000  
 Composition: t-butyl acrylate (34%), ethyl acrylate (35%), acrylic acid (21%), poly(dimethylsiloxane) (10%)  
 MWt of poly(dimethylsiloxane): 5,000
- (iii) poly(t-butyl acrylate-co-n-butyl acrylate-co-acrylic acid)-graft-poly(dimethylsiloxane)

MWt of copolymer: 150,000

Composition: t-butyl acrylate (47.25%), n-butyl acrylate (22.75%), acrylic acid (20%), poly(dimethylsiloxane) (10%)

MWt of poly(dimethylsiloxane): 10,000

- (iv) poly(t-butyl acrylate-co-2-methoxyethyl acrylate-co-methacrylic acid)-graft-poly(dimethylsiloxane)

MWt of copolymer: 100,000

Composition: t-butyl acrylate (27%), 2-methoxyethyl acrylate (43%), methacrylic acid (20%), poly(dimethylsiloxane) (10%)

MWt of poly(dimethylsiloxane): 15,000

- (v) poly(t-butyl acrylate-co-isobornyl acrylate-co-2-methoxyethyl acrylate-co-acrylic acid)-graft-poly(dimethylsiloxane)

MWt of copolymer: 95,000

Composition: t-butyl acrylate (33%), isobornyl acrylate (17%), 2-methoxyethyl acrylate (20%), acrylic acid (20%), poly(dimethylsiloxane) (10%)

MWt of poly(dimethylsiloxane): 10,000

- (vi) poly(t-butyl acrylate-co-lauryl methacrylate-co-acrylic acid)-graft-poly(dimethylsiloxane)

MWt of copolymer: 125,000

Composition: t-butyl acrylate (60%), lauryl methacrylate (10%), acrylic acid (20%), poly(dimethylsiloxane) (10%)

MWt of poly(dimethylsiloxane): 15,000

The Tg's for monomer units above can be found in The Polymer Handbook, third edition, (John Wiley & Sons, 1989) and the backbone Tg can be calculated using the method illustrated in Fundamental Principles of Polymeric Materials, second edition (John Wiley & Sons, 1993). Representative Tg's for monomers in the exemplary silicone grafted

polymers described above are as follows: The Tg of t-butyl acrylate is 44.85°C; the Tg of n-butyl acrylate is -54.15°C; the Tg of acrylic acid is 105.85°C; the Tg of methacrylic acid is 227.85°C; the Tg of ethyl acrylate is -24.15°C; the Tg of lauryl methacrylate is -65.15°C; and the Tg of 2-methoxyethyl acrylate is -50.15°C.

The silicone grafted polymers can be synthesized by free radical polymerization of the polysiloxane-containing monomers with the non-polysiloxane-containing monomers. The synthetic procedures are in general the same as those described for the adhesive copolymer. The silicone macromer is added in to the reactor along with the "A" and "B" monomers, and the reaction proceeds as for the adhesive copolymer examples. Compared to the adhesive copolymer, it may be necessary to choose different solvents for the polymerization reaction, as apparent to one skilled in the art, to keep the monomers and polymers in solution throughout the polymerization.

Without being limited by theory, it is believed that in forming the above-described silicone grafted polymers, there is some polymer which does not incorporate the silicone graft; such polymers have a relatively low weight average molecular weight e.g., below 20,000.

#### Personal Care Carrier

The compositions of the present invention comprise from about 0.1% to about 99.9%, preferably from about 0.5% to about 99.0% and most preferably from about 1.0% to about 99.9% of a suitable personal care carrier. Suitable carriers are fully described in U.S. Patent 5,061,481 issued October 29, 1991 to Suzuki et al., incorporated by reference herein. For example, skin care carriers typically comprise oil-in-water emulsions.

Hair spray compositions typically comprise a polar solvent phase as a liquid vehicle for the silicone grafted polymer. The polar solvent phases comprise one or more polar solvents that are present in the hair care compositions at a level of from about 80% to about 99%, preferably from

about 85% to about 98%, more preferably from about 90% to about 95% of the total composition.

The polar solvents essential to the present compositions are selected from the group consisting of water, C<sub>2</sub>-C<sub>3</sub> monohydric alkanols, and mixtures thereof. If present, C<sub>3</sub> alkanols, such as isopropanol, should be used at levels no greater than about 15% by weight of the composition, preferably no greater than about 12%, more preferably no greater than about 10%. High levels of C<sub>3</sub> monohydric alcohols are undesirable in the present compositions due to potential odor issues they can create. Preferred polar solvent phases contain water, ethanol, or mixtures thereof.

Where water and alcohol mixtures are used, for instance, water-ethanol or water-isopropanol-ethanol, the water content of the compositions is generally in the range of from about 0.5% to about 99%, preferably from about 5% to about 50% by weight of the total composition. In such mixtures, the alcohol solvents are generally present in the range of from 0.5% to about 99%, preferably from about 50% to about 95%, by weight of the total composition.

In yet another aspect of this invention are provided hair styling products, such as hair spray compositions, which contain reduced levels of volatile organic solvents. A reduced volatile organic solvent hair spray composition of the present invention contains no more than 80% volatile organic solvents (which include, for example, alkanols but not water). As used herein, volatile organic solvents means solvents which have at least one carbon atom and exhibit a vapor pressure of greater than 0.1 mm Hg at 20°C.

In the reduced volatile organic solvent hair styling products hereof, the compositions generally comprise at least 10%, by weight, of water. It is also specifically contemplated that they may contain at least about 11%, 12%, 13%, 14%, 15%, or more water.

The reduced volatile organic solvent compositions hereof will comprise up to about 90%, preferably up to about 70%, more preferably up

to about 60% even more preferably no more than about 50%, water; and from about 10% to about 80%, preferably from about 20% to about 80%, more preferably from about 40% to about 80%, of volatile organic solvent. It is also contemplated that the compositions can be limited to containing no more than about 75%, 65%, 55%, or other levels of volatile organic solvents.

Shampoos and rinse compositions typically comprise a volatile, nonpolar, branched chain hydrocarbon and is safe for topical application to the skin and hair. The branched chain hydrocarbon solvent hereof is present at a level of from about 0.1% to about 15%, preferably from about 0.5% to about 10%, more preferably from about 2% to about 8%, by weight of the composition. Also useful are low boiling point silicone oils.

The branched chain hydrocarbon solvent is characterized by a boiling point of at least about 105°C, preferably at least about 110°C, more preferably at least about 125°C, most preferably at least about 150°C. The boiling point is also generally about 260°C or less, preferably about 200°C or less. The hydrocarbon chosen should also be safe for topical application to the hair and skin.

The branched chain hydrocarbon solvents are selected from the group consisting of C<sub>10</sub>-C<sub>14</sub> branched chain hydrocarbons, and mixtures thereof, preferably C<sub>11</sub>-C<sub>13</sub> branched chain hydrocarbons, more preferably C<sub>12</sub> branched chain hydrocarbons. Saturated hydrocarbons are preferred, although it isn't necessarily intended to exclude unsaturated hydrocarbons.

Examples of suitable nonpolar solvents include isoparaffins of the above chain sizes. Isoparaffins are commercially available from Exxon Chemical Co. Examples include Isopar<sup>TM</sup> G (C<sub>10</sub>-C<sub>11</sub> isoparaffins), Isopar<sup>TM</sup> H and K (C<sub>11</sub>-C<sub>12</sub> isoparaffins), and Isopar<sup>TM</sup> L (C<sub>11</sub>-C<sub>13</sub> isoparaffins). The most preferred nonpolar solvent are C<sub>12</sub> branched chain hydrocarbons, especially isododecane. Isododecane is commercially available from Preperse, Inc. (South Plainfield, NJ, USA) as Permethyl<sup>TM</sup> 99A.

### Plasticizer

The compositions hereof can optionally contain a plasticizer for the silicone grafted polymer. Any plasticizer suitable for use in hair care products or for topical application to the hair or skin can be used. A wide variety of plasticizers are known in the art. These include acetyl triethylcitrate, triethylcitrate, glycerin, diisobutyl adipate, butyl stearate, and propylene glycol. Plasticizers are typically used at levels of from about 0.01% to about 10%, by weight of the composition, preferably from about 0.05% to about 3%, more preferably from about 0.05% to about 1%.

### Optional Components

#### Adhesive Polymer

The compositions of the present invention can comprise an additional adhesive polymer. The compositions hereof will generally comprise from about 0.1% to about 15%, preferably from 0.5% to about 8%, more preferably from about 1% to about 8%, by weight of the composition, of the adhesive polymer. It is not intended to exclude the use of higher or lower levels of the polymers, as long as an effective amount is used to provide adhesive or film-forming properties to the composition and the composition can be formulated and effectively applied for its intended purpose. By adhesive polymer what is meant is that when applied as a solution to a surface and dried, the polymer forms a film. Such a film will have adhesive and cohesive strength, as is understood by those skilled in the art.

The polymeric backbone is chosen such that it is compatible with the silicone adhesive styling polymer. By "compatible" is meant is that, when placed in a suitable solvent, the polymers form a stable solution, i. e., the polymers do not compete for solubility and therefore, cause no phase separation and when the solution is dried a uniform film is formed, with no macrophase separation of the two polymers. A suitable solvent is a solvent which substantially completely dissolves the non-silicone and silicone grafted polymers at the levels described herein. The polymer blend forms a relatively clear hairspray system (% transmittance at 450 nm is generally



greater than 80%). It is recognized that certain plasticizers can form cloudy films as well as incorrect neutralization levels. Therefore, this would fall outside this definition of compatibility. The compatibility can be tested by dissolving the adhesive polymer and the silicone grafted hair styling resin in a mutual solvent, and then evaporating the solvent to form a film. Incompatible polymers will form a cloudy film with poor mechanical properties, due to the large scale phase separation of the two polymers. Alternatively, after drying the polymer solution to a film, compatibility can be evaluated by measuring the Tg. Compatible polymers will have a single Tg, while incompatible polymers will exhibit two Tg's. Although compatibility can occur between two polymers of completely different structures, it is preferred that compatibility be obtained by making the composition of the non-silicone backbone of the silicone grafted polymer similar to or identical to the composition of the adhesive polymer.

The adhesive polymer should have a weight average molecular weight of at least about 20,000, preferably greater than about 25,000, more preferably greater than about 30,000, most preferably greater than about 35,000. There is no upper limit for molecular weight except that which limits applicability of the invention for practical reasons, such as processing, aesthetic characteristics, formulateability, etc. In general, the weight average molecular weight will be less than about 10,000,000, more generally less than about 5,000,000, and typically less than about 2,000,000. Preferably, the weight average molecular weight will be between about 20,000 and about 2,000,000, more preferably between about 30,000 and about 1,000,000, and most preferably between about 40,000 and about 500,000.

Preferably, the adhesive hereof when dried to form a film have a Tg of at least about -20°C, more preferably at least about 20°C, so that they are not unduly sticky, or "tacky" to the touch. As used herein, the abbreviation "Tg" refers to the glass transition temperature of the backbone of the

polymer. Preferably, the Tg is above about -20°C, more preferably above about 20°C.

Preferably the weight ratio of the non-silicone polymer to silicone grafted polymer ranges from about 1:10 to about 1:1, preferably from about 1:5 to about 1:1.

Exemplary adhesive polymers for use in the present invention include the following, where the numbers following the structure indicate the weight ratios of monomers as loaded into the polymerization reactor:

- (i) acrylic acid/t-butyl acrylate 25/75
- (ii) dimethylaminoethyl methacrylate/isobutyl methacrylate/2-ethylhexyl-methacrylate 40/40/20
- (iii) t-butylacrylate/acrylic acid 65/35
- (iv) polymer (ii) quaternized by treatment with methyl chloride

The adhesive polymers can be synthesized as described above such as by free radical polymerization of the monomers.

Solubility of the adhesive polymer, as described above, should be determined after neutralization, if any, as well as after addition of other ingredients that may be included in the polar solvent phase, such as surfactants, solubilizers, etc.

The present compositions can contain a wide variety of additional optional ingredients, including among them any of the types of ingredients known in the art for use in hair setting compositions, especially hair spray compositions and hair setting tonics. These ingredients include, but are not limited to, surfactants (including fluorinated surfactants and silicone copolyols), and ionic strength modifiers, propellants, hair conditioning agents (e.g., silicone fluids, fatty esters, fatty alcohols, long chain hydrocarbons, cationic surfactants, etc.)

#### Ionic Strength Modifier System

Optionally, the compositions of the present invention can contain an effective amount of a non-surface active ionic strength modifier system for reducing the viscosity of the hair spray composition. When used, the ionic

strength modifiers will be present in the present compositions at a level of at least about 0.01%, by weight of the composition. The upper limit is dependent upon the maximum amount of the ionic strength modifiers that can be present in the particular compositions hereof such that the hair setting resin remains solubilized or dispersed. As will be understood by those skilled in the art, as the ionic strength of the composition is increased, the resin will eventually fall out of solution, or otherwise no longer remain solubilized or dispersed in the polar liquid carrier. The upper limit of the ionic strength modifier system level will vary depending upon the particular ionic strength modifiers, liquid vehicle, resin, and other ingredients present in the composition. Thus, for example, the maximum amount of the ionic strength modifiers that can be used will tend to be lower for compositions with liquid vehicles containing less water, compared to compositions with more water. Generally, the compositions will comprise about 4%, by weight, or less of the ionic strength modifiers, more generally about 2% or less, and typically about 1% or less. Preferably, the compositions hereof will comprise from about 0.01% to about 0.5%, more preferably from about 0.01% to about 0.1%, of the ionic strength modifier system.

The ionic strength modifier system comprises a mixture of monomeric cations and anions. The ions of the ionic strength modifier system hereof are non-surface active, i.e. they do not significantly reduce surface tension. For purposes hereof, non-surface active shall mean the ions, which at a 0.5% aqueous solution concentration, reduce surface tension by no more than 5.0 dynes/cm<sup>2</sup>. Generally, the ions of the ionic strength modifier system hereof will be characterized by having, at maximum, four or less carbon atoms per charge, preferably two or less carbon atoms, in any aliphatic chain or straight or branched chain organic heterochain.

The ionic strength modifier system comprises monomeric ions of the type which are products of acid-base reactions. Thus, basic and acidic ions OH<sup>-</sup> and H<sup>+</sup> do not constitute part of the ionic strength modifier system hereof, although they may be present in the composition. The ions hereof

are incorporated into the composition in a form such that they can exist in the composition as free ions, i.e., in dissociated form. It is not necessary that all of the ions added exist in the composition as free ions, but must be at least partially soluble or dissociated in the composition. The ionic strength modifiers can be incorporated into the hair styling compositions, for example, by addition of soluble salts, or by addition of mixtures of acids and bases, or by a combination thereof. It is a necessary aspect of the invention that both anions and cations of the ionic strength modifier system be included in the composition.

Suitable cations for use include, for example, alkali metals, such as lithium, sodium, and potassium, and alkaline-earth metals, such as magnesium, calcium, and strontium. Preferred of the divalent cations is magnesium. Preferred monovalent metal ions are lithium, sodium, and potassium, particularly sodium and potassium. Suitable means of addition to the compositions hereof include, for example, addition as bases, e.g., hydroxides, sodium hydroxide and potassium hydroxide, and such as salts that are soluble in the liquid carrier, e.g. salts of monomeric anions such as those described below.

Other suitable cations include organic ions, such as quaternary ammonium ions and cationic amines, such as ammonium mono-, di-, and tri-ethanolamines, triethylamine, morpholine, aminomethylpropanol (AMP), aminoethylpropanediol, etc. Ammonium and the amines are preferably provided in the forms of salts, such as hydrochloride salts.

Monomeric anions that can be used include halogen ions, such as chloride, fluoride, bromide, and iodide, particularly chloride, sulfate, ethyl sulfate, methyl sulfate, cyclohexyl sulfamate, thiosulfate, toluene sulfonate, xylene sulfonate, citrate, nitrate, bicarbonate, adipate, succinate, saccharinate, benzoate, lactate, borate, isethionate, tartrate, and other monomeric anions that can exist in dissociated form in the hair styling composition. The anions can be added to the compositions hereof, for example, in the form of acids or salts which are at least partially soluble in

the liquid vehicle, e.g., sodium or potassium salts of acetate, citrate, nitrate, chloride, sulfate, etc. Preferably, such salts are entirely soluble in the vehicle.

The use of ionic strength modifiers are especially useful in reduced volatile organic solvent compositions, most especially those utilizing silicone macromer-containing polymers.

#### Personal Care Compositions

The present invention encompasses a wide variety of personal care compositions, including shampoos, soaps, lotions, creams, antiperspirants, nail enamels, lipsticks, foundations, mascaras, sunscreens, hair spray compositions, mousses, and hair setting tonics. Compositions that will be flowable, e.g., low viscosity compositions that, preferably, are suitable for spray application as well as higher viscosity compositions are also contemplated.

Personal care carriers are suitable for use in the present invention are described in U.S. Patent 5,306,485 to Robinson et al., issued April 26, 1994, and U.S. Patent 5,002,680 to Schmidt et al., issued March 26, 1991, both of which are incorporated by reference herein. Hair spray compositions and mousses of the present invention can be dispensed from containers which are aerosol dispensers or pump spray dispensers. Such dispensers, i.e., containers, are well known to those skilled in the art and are commercially available from a variety of manufacturers, including American National Can Corp. and Continental Can Corp.

When the hair spray compositions are to be dispensed from a pressurized aerosol container, a propellant which consists of one or more of the conventionally-known aerosol propellants may be used to propel the compositions. A suitable propellant for use can be generally any liquifiable gas conventionally used for aerosol containers.

Suitable propellants for use are volatile hydrocarbon propellants which can include liquefied lower hydrocarbons of 3 to 4 carbon atoms such as propane, butane and isobutane. Other suitable propellants are

hydrofluorocarbons such as 1,2-difluoroethane (Hydrofluorocarbon 152A) supplied as Dymel 152A by DuPont. Other examples of propellants are dimethylether, N-butane, isobutane, propanes, nitrogen, carbon dioxide, nitrous oxide and atmospheric gas and mixtures thereof.

The aerosol propellant may be mixed with the present compositions and the amount of propellant to be mixed is governed by normal factors well known in the aerosol art. Generally, for liquifiable propellants, the level of propellant is from about 10% to about 60% by weight of the total composition, preferably from about 15% to about 40% by weight of the total composition.

Alternatively, pressurized aerosol dispensers can be used where the propellant is separated from contact with the hair spray composition such as a two compartment can of the type sold under the tradename SEPRO from American National Can Corp.

Other suitable aerosol dispensers are those characterized by the propellant being compressed air which can be filled into the dispenser by means of a pump or equivalent device prior to use. Such dispensers are described in U.S. Patents 4,077,441, March 7, 1978, Olofsson and 4,850,577, July 25, 1989, TerStege, both incorporated by reference herein, and in U.S. Serial No. 07/839,648, Gosselin et al., filed February 21, 1992, also incorporated by reference herein. Compressed air aerosol containers suitable for use are also currently marketed by The Procter & Gamble Company under their tradename VIDAL SASSOON AIRSPRAY® hair sprays.

Conventional non-aerosol pump spray dispensers, i.e., atomizers, can also be used.

Other hair styling compositions include tonics and lotions, which are typically dispensed in a conventional bottle or tube, and applied directly to the hair or first dispensed to the hand and then to the hair.

The hair styling formulations of the present invention can optionally contain conventional hair care composition adjuvants. Generally, adjuvants

collectively can comprise from about 0.05% to about 5% by weight and preferably from about 0.1% to about 3%, by weight. Such conventional optional adjuvants are well known to those skilled in the art and include in addition to those discussed above, emollients; lubricants and penetrants such as various lanolin compounds; protein hydrolysates and other protein derivatives; ethylene adducts and polyoxyethylene cholesterol; dyes, tints, bleaches, reducing agents and other colorants; pH adjusting agents sunscreens; preservatives; thickening agents (e.g. polymeric thickeners, such as xanthan gum); and perfume.

#### METHOD OF MAKING

The personal care compositions of the present invention can be made using conventional formulation and mixing techniques.

#### METHOD OF USE

The compositions of the present invention are used in conventional ways to provide the personal care compositions of the present invention. Such method generally involves application of an effective amount of the product. For example, in a hair spray composition, said composition is applied to the desired dry, slightly damp, or wet hair before and/or after the hair is arranged to a desired style. The composition is then dried or allowed to dry. By "effective amount" is meant an amount sufficient to provide the desired benefits.

The following Experimentals and Examples further illustrate embodiments within the scope of the present invention. They are given solely for the purposes of illustration and are not to be construed as limitations of the present invention as many variations of the invention are possible without departing from its spirit and scope.

#### EXPERIMENTALS

The following synthesis exemplify silicone grafted polymers useful in the present compositions.

##### *Polymer 1*

*Synthesis of Poly(t-butyl acrylate-co-n-butyl acrylate-co-acrylic acid-co-methacrylic acid)-graft-poly(dimethylsiloxane)*

Place 42.75 parts of t-butyl acrylate, 27.25 parts n-butyl acrylate, 10 parts methacrylic acid, 10 parts acrylic acid, and 10 parts polydimethylsiloxane macromonomer in a roundbottom flask. Add sufficient acetone as the reaction solvent to produce a final monomer concentration of 20%. Purge the vessel with argon for approximately one hour. Following the purge, maintain a constant positive pressure on the closed reaction system with argon. Heat the reaction to 58°C. Prepare a 10% solution of azobisisobutyronitrile (0.5% by weight relative to the amount of monomer) in acetone, and add it to the reaction mixture. Maintain heat and stirring for 20 hours. Terminate the reaction by opening the reactor to atmosphere and cooling to room temperature.

The polymer solution is then precipitated in water at one part solution to 15 parts water. The resultant polymer is then redissolved in acetone. This procedure is repeated six times, with the final polymer being placed in a vacuum oven for heated drying. This completes the polymer purification process.

**Polymer 2**

*Synthesis of Poly(t-butyl acrylate-co-n-butyl acrylate-co-methacrylic acid)-graft-poly(dimethylsiloxane)*

Place 32 parts of t-butyl acrylate, 27 parts n-butyl acrylate, 21 parts methacrylic acid, and 20 parts polydimethylsiloxane macromonomer in a roundbottom flask. Add sufficient acetone as the reaction solvent to produce a final monomer concentration of 20%. Purge the vessel with argon for approximately one hour. Following the purge, maintain a constant positive pressure on the closed reaction system with argon. Heat the reaction to 58°C. Prepare a 10% solution of azobisisobutyronitrile (0.5% by weight relative to the amount of monomer) in acetone, and add it to the reaction mixture. Maintain heat and stirring for 20 hours. Terminate the



reaction by opening the reactor to atmosphere and cooling to room temperature.

The polymer solution is then precipitated in water at one part solution to 15 parts water. The resultant polymer is then redissolved in acetone. This procedure is repeated six times, with the final polymer being placed in a vacuum oven for heated drying. This completes the polymer purification process.

## EXAMPLES

### Examples 1-4

The following examples represent nonaerosol hairspray compositions of the present invention.

	<u>Example No</u>			
Component (wt. %)	1	2	3	4
Copolymer <sup>1</sup>	4.00	4.75	5.50	5.50
Isododecane <sup>2</sup>	1.00	1.00	1.00	3.00
Diisopropyl butyl adipate	0.40	0.75	0.90	0.55
Sodium hydroxide <sup>3</sup>	0.96	1.20	1.44	1.6
Perfume	0.10	0.10	0.10	0.10
Water	17.00	20.00	20.00	18.00
Ethanol <sup>4</sup>	76.54	71.95	70.56	71.25

<sup>1</sup> Poly(t-butyl acrylate-co-n-butyl acrylate-co-acrylic acid-co-methacrylic acid)-graft-poly(dimethylsiloxane).

<sup>2</sup> PERMETHYL 99A, from Presperse, Inc., South Plainfield, NJ, USA.

<sup>3</sup> Sodium hydroxide is 30% active.

<sup>4</sup> SDA 40 (100% ethanol).

EXAMPLE 5Sunscreen Composition

An oil-in-water emulsion is prepared by combining the following components utilizing conventional mixing techniques.

Ingredients

<u>Phase A</u>	<u>Weight %</u>
Water	QS100
Carbomer 954[1]	0.24
Carbomer 1342[2]	0.16
Copolymer[3]	1.00
Disodium EDTA	0.05
<u>Phase B</u>	
Isoarachidyl Neopentanoate[4]	2.00
PVP Eicosene Copolymer[5]	2.00
Octyl Methoxycinnamate	7.50
Octocrylene	4.00
Oxybenzone	1.00
Titanium Dioxide	2.00
Cetyl Palmitate	0.75
Stearoxytrimethylsilane (and)	
Stearyl Alcohol[6]	0.50
Glyceryl Tribehenate	0.75
Dimethicone	1.00
Tocopheryl Acetate	0.10
DEA-Cetyl Phosphate	0.20
<u>Phase C</u>	
Water	2.00
Triethanolamine 99%	0.60
NaOH solution 40%	0.33
<u>Phase D</u>	
Water	2.00

Butylene Glycol	2.00
DMDM Hydantoin (and)	
Iodopropynyl Butylcarbamate <sup>[7]</sup>	0.25
dL Panthenol	1.00
<u>Phase E</u>	
dimethylmyristamine	0.36

- [1] Available as Carbopol® 954 from B.F. Goodrich.
- [2] Available as Carbopol® 1342 from B.F. Goodrich.
- [3] Poly(t-butyl acrylate-co-n-butyl acrylate-co-acrylic acid-co-methacrylic acid)-graft-poly(dimethylsiloxane)
- [4] Available as Ganex V-220 from GAF Corporation.
- [5] Available as DC 580 Wax from Dow Corning.
- [6] Available as Synchronowax HRC from Croda.
- [7] Available as Glydant Plus from Lonza.

In a suitable vessel the Phase A ingredients are dispersed in the water and heated to 75-85°C. In a separate vessel the Phase B ingredients (except DEA-Cetyl Phosphate) are combined and heated to 85-90°C until melted. Next, the DEA-Cetyl Phosphate is added to the liquid Phase B and stirred until dissolved. This mixture is then added to Phase A to form the emulsion. The Phase C ingredients are combined until dissolved and then added to the emulsion. The emulsion is then cooled to 40-45°C with continued mixing. In another vessel, the Phase D ingredients are heated with mixing to 40-45°C until a clear solution is formed and this solution is then added to the emulsion. Finally, the emulsion is cooled to 35°C and the Phase E ingredients are combined at 65°C, use an appropriate homogenizer to facilitate incorporation of the copolymer into the solvent. Phase E is the cooled to 35°C, added and mixed.

This emulsion is useful for topical application to the skin to provide protection from the harmful effects of ultraviolet radiation.

EXAMPLE 6Facial Moisturizer

A leave-on facial emulsion composition containing a cationic hydrophobic surfactant is prepared by combining the following components utilizing conventional mixing techniques.

<u>Ingredient</u>	<u>Weight %</u>
Phase A	
Water	QS100
Glycerin	3.00
Cetyl Palmitate	3.00
Cetyl Alcohol	1.26
Quaternium-22	1.00
Glyceryl Monohydroxy Stearate	0.74
Dimethicone	0.60
Stearic Acid	0.55
Octyldodecyl Myristate	0.30
Potassium Hydroxide	0.20
Carbomer 1342	0.125
Tetrasodium EDTA	0.10
DMDM Hydantoin and Iodopropynyl	
Butyl Carbamate	0.10
Carbomer 951	0.075
Phase B	
Isododecane	4.00
Copolymer <sup>[1]</sup>	1.00
stearamine	0.36

[1] Poly(t-butyl acrylate-co-n-butyl acrylate-co-acrylic acid-co-methacrylic acid)-graft-poly(dimethylsiloxane)

In a suitable vessel the Phase A ingredients are combined to form an emulsion. Phase B is prepared by dispersing the copolymer in Isododecane (solvent) then adding the stearamine. Heat the solution to 65°C and use an

appropriate homogenizer to facilitate incorporation of the copolymer into the solvent. Cool the Phase B and mix into Phase A using conventional mixing techniques.

This emulsion is useful for application to the skin as a moisturizer.

#### EXAMPLE 7

The following is an anti-perspirant composition representative of the present invention.

<b>Component</b>	<b>Weight %</b>
PPG 2 Myristyl Propionate	34.00 %
Glyceryl C <sub>18</sub> - C <sub>36</sub> Wax Acid Ester	0.40 %
Cyclomethicone	32.75 %
Copolymer[1]	1.00 %
dimethylmyristamine	0.50 %
Aluminum Chlorohydrate	19.00 %
PPG 5 Ceteth 20	7.50 %
Water	1.50 %

[1] Poly(t-butyl acrylate-co-n-butyl acrylate-co-acrylic acid-co-methacrylic acid)-graft-poly(dimethylsiloxane)

Mix PPG 2 Myristyl Propionate and Glyceryl C<sub>18</sub> - C<sub>36</sub> Wax Acid Ester, heat to 75°C. Disperse the Chlorohydrate. Disperse the copolymer in Cyclomethicone (solvent) then add the dimethylmyristamine. Heat the solution to 65°C and use an appropriate homogenizer to facilitate incorporation of the copolymer into the solvent. Add the cyclomethicone mixture to the Chlorohydrate dispersion. Mix PPG 5 Ceteth 20 and the water, then add to oils, perfume and cool.

**EXAMPLE 8**

The following is an anti-acne composition representative of the present invention.

<b>Component</b>	<b>Weight %</b>
<u>Copolymer-Solvent Mix</u>	
Copolymer <sup>[1]</sup>	1.00 %
dimethylpalmitamine	0.18 %
Isopar H® <sup>[2]</sup>	3.75 %
<u>Main Mix</u>	
Water	Q.S. to 100 %
Ethanol (SDA 40)	40.00 %
Carbopol 940®	0.75 %
Triethanol Amine	1.00 %
Salicylic Acid	2.00 %

<sup>[1]</sup>Poly(t-butyl acrylate-co-n-butyl acrylate-co-acrylic acid-co-methacrylic acid)-graft-poly(dimethylsiloxane)

<sup>[2]</sup>C<sub>11</sub>-C<sub>12</sub> Isoparaffin, available from Exxon Chemical Co.

This product is prepared by dispersing the copolymer in Isopar H® (solvent) then adding the dimethylpalmitamine. Heat the solution to 65°C and use an appropriate homogenizer to facilitate incorporation of the copolymer into the solvent. The other components are mixed in a separate vessel at ambient temperature. The copolymer-solvent premix is cooled (if needed) and added to the other components. This composition is useful for application to the skin to provide improve water resistance and is useful in the treatment of acne.

EXAMPLE 9

The following is an anti-acne composition representative of the present invention.

Component	Weight %
<u>Copolymer-Solvent Mix</u>	
Copolymer <sup>[1]</sup>	1.00 %
dimethylpalmitamine	0.18 %
Isopar H® <sup>[2]</sup>	3.75 %
<u>Main Mix</u>	
Water	Q.S. to 100 %
Ethanol (SDA 40)	20.00 %
Carbopol 940®	0.75 %
Triethanol Amine	1.00 %
Ibuprofen	2.00 %

[1] Poly(t-butyl acrylate-co-n-butyl acrylate-co-acrylic acid-co-methacrylic acid)-graft-poly(dimethylsiloxane)

[2] C<sub>11</sub>-C<sub>12</sub> Isoparaffin, available from Exxon Chemical Co.

This product is prepared by dispersing the copolymer in Isopar H® (solvent) then adding the dimethylpalmitamine. Heat the solution to 65°C and use an appropriate homogenizer to facilitate incorporation of the copolymer into the solvent. The other components are mixed in a separate vessel at ambient temperature. The copolymer-solvent premix is cooled (if needed) and added to the other components. This composition is useful for application to the skin to provide improve water resistance and is useful for the analgesic effects.

## WHAT IS CLAIMED IS:

1. A personal care composition comprising:
  - (a) a silicone grafted adhesive polymer, said polymer being characterized by an organic polymeric backbone wherein said backbone comprises
    - (i) at least one monomer wherein when said monomer is polymerized as a homopolymer having a Tg of from about -120° C to about 25° C and
    - (ii) at least one monomer wherein when said monomer is polymerized as a homopolymer having a Tg of from above about 25°C to about 250°Cwherein said silicone grafted adhesive polymer has silicone macromers grafted to said backbone and wherein the number average molecular weight of said silicone macromers is greater than about 1000; and
  - (b) a personal care carrier.
2. A personal care composition according to Claim 1, wherein said monomer of (a) and (b) is independently selected from the group consisting of acrylic acid, methacrylic acid, N,N-dimethylacrylamide, dimethyl aminoethyl methacrylate, quaternized dimethylaminoethyl methacrylate, methacrylamide, N-t-butyl acrylamide, maleic acid, maleic anhydride and its half esters, crotonic acid, itaconic acid, acrylamide, acrylate alcohols, hydroxyethyl methacrylate, diallyldimethyl ammonium chloride, vinyl pyrrolidone, vinyl ethers, maleimides, vinyl pyridine, vinyl imidazole, styrene sulfonate, allyl alcohol, vinyl alcohol, esters of C<sub>1</sub>-C<sub>18</sub> alcohols, styrene; vinyl acetate; vinyl chloride; vinylidene chloride; vinyl propionate; alpha-



methystyrene; t-butylstyrene; butadiene; cyclohexadiene; ethylene; propylene; vinyl toluene and salts of acids and amines above.

3. A personal care composition according to Claim 2 wherein the monomer of (a) is selected from the group consisting of 3-methoxybutyl acrylate, 2-methoxyethyl acrylate, 2-phenoxyethyl ester, 2-hydroxyethyl ester, 4-hydroxybutyl acrylate, 2-ethoxyethoxyethyl acrylate, 2-ethoxyethyl acrylate, n-butyl acrylate, dodecyl acrylate, 2-ethylhexyl acrylate, 2-ethylbutyl acrylate, n-ethyl acrylate, n-heptyl acrylate, n-hexyl acrylate, iso-butyl acrylate, iso-decyl acrylate, iso-propyl acrylate, 3-methylbutyl acrylate, 2-methylpentyl acrylate, nonyl acrylate, octyl acrylate, 2-ethylhexyl methacrylate, n-pentyl methacrylate, N-dodecylacrylamide, N-octadecylacrylamide, sec-butyl vinyl ether, butyl vinyl ether, vinyl propionate, vinyl butyrate, decylvinyl ether, methyl vinyl ether, 4-decylstyrene, isobutylene, 1-butene, 5-methyl-1-hexene, isoprene, 1,2-butadiene, 1,4-butadiene and mixtures thereof.
4. A personal care composition according to Claim 3 wherein the monomer of (a) is selected from the group consisting of 3-methoxybutyl acrylate, 2-methoxyethyl acrylate, n-butyl acrylate, dodecyl acrylate, 2-ethylhexyl acrylate, 2-ethylbutyl acrylate, ethyl acrylate, n-heptyl acrylate, n-hexyl acrylate, iso-butyl acrylate, iso-decyl acrylate, iso-propyl acrylate, 3-methylbutyl acrylate, 2-methylpentyl acrylate, nonyl acrylate, octyl acrylate, 2-ethylhexyl methacrylate, n-pentyl methacrylate, N-octadecylacrylamide and mixtures thereof.

5. A personal care composition according to Claim 4 wherein the monomer of (a) is selected from the group consisting of 2-methoxyethyl acrylate, n-butyl acrylate, n-ethyl acrylate and mixtures thereof.
6. A personal care composition according to Claim 3 wherein the monomer of (a) has a Tg of from about -70° C to about 25° C.
7. A personal care composition according to Claim 6 wherein the monomer of (a) has a Tg of from about -60° C to about 0° C.
8. A personal care composition according to Claim 7 wherein the monomer of (a) has a Tg of from about -60° C to about -20° C.
9. A personal care composition according to Claim 2 wherein the monomer of (b) is selected from the group consisting of sec-butyl methacrylate, t-butyl acrylate, methyl methacrylate, isopropyl methacrylate, 2-t-butylaminoethyl methacrylate, dimethyl aminoethyl methacrylate, quaternized dimethyl aminoethyl methacrylate, 4-biphenyl acrylate, pentachlorophenyl acrylate, 3,5-dimethyladamantyl acrylate, 3,5-dimethyladamentyl methacrylate, isobornyl acrylate, trimethysilyl methacrylate, trimethylsilyl acrylate, acrylic acid, methacrylic acid, salts of acrylic and methacrylic acids, N-butylacrytlamide, acrylamide, N-isopropylacrylamide, N-t-butylmethacrylamide, 2-vinylpyridine, 4-vinylpyridine, vinyl acetate, vinyl chloride, N-vinylcaprolactam, N-vinyl pyrrolidone, cyclohexyl vinyl ether, vinyl alcohol, vinyl imidazole, styrene, 4-t-butylstyrene, 2-methoxystyrene, 4-acetylstyrene, styrene sulfonate, diallyldimethylammonium chloride, maleimides, crotonic acid, itaconic acid, maleic anhydrides, allyl alcohol,  $\alpha$ -pinene,  $\beta$ -pinene, tert-butyl

styrene,  $\alpha$ -methyl styrene, indene, norbornene, norbornylene and mixtures thereof.

10. A personal care composition according to Claim 9 wherein the monomer of (b) is selected from the group consisting of t-butyl methacrylate, t-butyl acrylate, methyl methacrylate, dimethyl aminoethyl methacrylate, isopropyl methacrylate, trimethylsilyl methacrylate, trimethylsilyl acrylate, acrylic acid, methacrylic acid, salts of acrylic and methacrylic acids, tert-butyl styrene,  $\alpha$ -methyl styrene, 2-vinylpyridine, 4-vinylpyridine, N-isopropylacrylamide, N-t-butylmethacrylamide and mixtures thereof.
11. A personal care composition according to Claim 10 wherein the monomer of (b) is selected from the group consisting of t-butyl methacrylate, t-butyl acrylate, methyl methacrylate, acrylic acid, methacrylic acid, salts of acrylic and methacrylic acids, tert-butyl styrene.
12. A personal care composition according to Claim 9 wherein the monomer of (b) has a Tg of from above about 30° C to about 200° C.
13. A personal care composition according to Claim 12 wherein the monomer of (b) has a Tg of from about 35° C to about 150° C.
14. A personal care composition according to Claim 11 wherein the monomer of (b) has a Tg of from about 40° C to about 130° C.

15. A personal care composition according to Claim 4 wherein said copolymer is formed from the random copolymerization of the following relative weight percentages of vinyl monomer units and polysiloxane-containing macromonomer units:

- a. from about 50% to about 98%, by weight of said copolymer, of vinyl monomer units, and
- b. from about 2% to about 50%, by weight of said copolymer, of polysiloxane-containing macromonomer units, wherein said polysiloxane-containing macromonomer units have a weight average molecular weight from about 1,000 to about 50,000, and correspond to the chemical formula:

$X(Y)_nSi(R)_{3-m}(Z)_m$  wherein:

X is a vinyl group copolymerizable with said vinyl monomer units;

Y is a divalent linking group;

R is selected from the group consisting of hydrogen, hydroxyl, C1-C6 alkyl, C1-C6 alkoxy, C2-C6 alkylamino, phenyl, C1-C6 alky or alkoxy-substituted phenyl;

Z is a monovalent siloxane polymeric moiety having a number average molecular weight of at least about 1000, is essentially unreactive under copolymerization conditions, and is pendant from said vinyl polymeric backbone after polymerization;

n is 0 or 1; and

m is an integer from 1 to 3.

16. A personal care composition according to Claim 8 wherein said copolymer is formed from the random copolymerization of the following relative weight percentages of vinyl monomer units and polysiloxane-containing macromonomer units:

- a. from about 50% to about 98%, by weight of said copolymer, of vinyl monomer units, and

- b. from about 2% to about 50%, by weight of said copolymer, of polysiloxane-containing macromonomer units, wherein said polysiloxane-containing macromonomer units have a weight average molecular weight from about 1,000 to about 50,000, and correspond to the chemical formula:

$X(Y)_nSi(R)_{3-m}(Z)_m$  wherein:

X is a vinyl group copolymerizable with said vinyl monomer units;

Y is a divalent linking group;

R is selected from the group consisting of hydrogen, hydroxyl, C1-C6 alkyl, C1-C6 alkoxy, C2-C6 alkylamino, phenyl, C1-C6 alky or alkoxy-substituted phenyl;

Z is a monovalent siloxane polymeric moiety having a number average molecular weight of at least about 1000, is essentially unreactive under copolymerization conditions, and is pendant from said vinyl polymeric backbone after polymerization;

n is 0 or 1; and

m is an integer from 1 to 3.

17. A personal care composition according to Claim 1 in the form of a shampoo, soap, lotion, cream, antiperspirant, nail enamel, lipstick, foundation, mascara, sunscreen, hair spray, mousse or hair setting tonic.
18. A hairspray composition comprising
- (a) a silicone grafted adhesive polymer, said polymer being characterized by an organic polymeric backbone wherein said backbone comprises
    - (i) at least one monomer wherein when said monomer is polymerized as a homopolymer having a Tg of from about -120° C to about 25° C and

(ii) at least one monomer wherein when said monomer is polymerized as a homopolymer having a Tg of from above about 25° C to about 250° C

wherein said silicone grafted adhesive polymer has silicone macromers grafted to said backbone and wherein the number average molecular weight of said silicone macromers is greater than about 1000; and

(b) a solvent carrier.

19. A hairspray composition according to Claim 17, wherein said monomer of (a) and (b) is independently selected from the group consisting of acrylic acid, methacrylic acid, N,N-dimethylacrylamide, dimethyl aminoethyl methacrylate, quaternized dimethylaminoethyl methacrylate, methacrylamide, N-t-butyl acrylamide, maleic acid, maleic anhydride and its half esters, crotonic acid, itaconic acid, acrylamide, acrylate alcohols, hydroxyethyl methacrylate, diallyldimethyl ammonium chloride, vinyl pyrrolidone, vinyl ethers, maleimides, vinyl pyridine, vinyl imidazole, styrene sulfonate, allyl alcohol, vinyl alcohol, esters of C<sub>1</sub>-C<sub>18</sub> alcohols, styrene; polystyrene macromer; vinyl acetate; vinyl chloride; vinylidene chloride; vinyl propionate; alpha-methylstyrene; t-butylstyrene; butadiene; cyclohexadiene; ethylene; propylene; vinyl toluene and salts of acids and amines above and wherein the monomer of (a) has a Tg of from about -60° C to about -20° C .
20. A hairspray composition according to Claim 17 wherein the monomer of (b) is selected from the group consisting of sec-butyl methacrylate, t-butyl acrylate, methyl methacrylate, isopropyl methacrylate, 2-t-butylaminoethyl methacrylate, dimethyl aminoethyl methacrylate, quaternized dimethyl aminoethyl methacrylate, 4-biphenyl acrylate, pentachlorophenyl acrylate, 3,5-dimethyladamantyl acrylate, 3,5-

dimethyladamentyl methacrylate, isobornyl acrylate, trimethylsilyl methacrylate, trimethylsilyl acrylate, acrylic acid, methacrylic acid, salts of acrylic and methacrylic acids, N-butylacrylamide, acrylamide, N-isopropylacrylamide, N-t-butylmethacrylamide, 2-vinylpyridine, 4-vinylpyridine, vinyl acetate, vinyl chloride, N-vinylcaprolactam, N-vinyl pyrrolidone, cyclohexyl vinyl ether, vinyl alcohol, vinyl imidazole, styrene, 4-t-butylstyrene, 2-methoxystyrene, 4-acetylstyrene, styrene sulfonate, diallyldimethylammonium chloride, maleimides, crotonic acid, itaconic acid, maleic anhydrides, allyl alcohol,  $\alpha$ -pinene,  $\beta$ -pinene, tert-butyl styrene,  $\alpha$ -methyl styrene, indene, norbornene, norbornylene and mixtures thereof and wherein the monomer of (b) has a Tg of from about 35° C to about 150° C.

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 98/08285

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 A61K7/48 A61K7/06

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 A61K C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 388 582 A (KOBAYASHI KOSE CO) 26 September 1990 see example 1 ---	1-20
X	US 4 981 902 A (GARBE JAMES E ET AL) 1 January 1991 see column 11, line 56 - column 12, line 41; claims 1-11 ---	1-16
X	EP 0 391 273 A (SHIONOGI & CO ;NISSHIN KAGAKU KOGYO KK (JP)) 10 October 1990 see examples ---	1-17
X	EP 0 408 311 A (MITSUBISHI PETROCHEMICAL CO) 16 January 1991 see examples 3,4 --- -/-	1-20

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance  
 "E" earlier document but published on or after the international filing date  
 "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)  
 "O" document referring to an oral disclosure, use, exhibition or other means  
 "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention  
 "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone  
 "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.  
 "&" document member of the same patent family

Date of the actual completion of the international search

18 August 1998

Date of mailing of the international search report

02/09/1998

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
 NL - 2280 HV Rijswijk  
 Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
 Fax: (+31-70) 340-3016

Authorized officer

Meulemans, R



# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 98/08285

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 769 290 A (OREAL) 23 April 1997 see page 3, line 10 - page 5, line 16 ---	1-20
X	WO 95 00106 A (PROCTER & GAMBLE ;WELCH ROSEMARY JANE (GB); DODSWORTH EMMA LOUISE) 5 January 1995 see claim 8 ---	1-20
X	WO 93 03705 A (PROCTER & GAMBLE) 4 March 1993 see page 17, line 24-28 -----	1-20

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 98/08285

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0388582 A	26-09-1990	JP 2247110 A	02-10-1990
		JP 2741237 B	15-04-1998
		JP 2250812 A	08-10-1990
		JP 2132141 A	21-05-1990
		JP 2700816 B	21-01-1998
		JP 2258709 A	19-10-1990
		JP 2279617 A	15-11-1990
		DE 69014358 D	12-01-1995
		DE 69014358 T	14-06-1995
		US 5061481 A	29-10-1991
		US 5219560 A	15-06-1993
		JP 3008432 A	16-01-1991
US 4981902 A	01-01-1991	US RE34902 E	11-04-1995
		US 4988506 A	29-01-1991
EP 0391273 A	10-10-1990	JP 2262511 A	25-10-1990
		JP 2740541 B	15-04-1998
		DE 69006242 D	10-03-1994
		DE 69006242 T	05-05-1994
		DK 391273 T	28-02-1994
		ES 2062147 T	16-12-1994
		US 5229435 A	20-07-1993
EP 0408311 A	16-01-1991	DE 69028742 D	07-11-1996
		JP 3128909 A	31-05-1991
		US 5480634 A	02-01-1996
		US 5166276 A	24-11-1992
EP 0769290 A	23-04-1997	FR 2739283 A	04-04-1997
		JP 9110632 A	28-04-1997
WO 9500106 A	05-01-1995	AU 7200594 A	17-01-1995
WO 9303705 A	04-03-1993	AT 139436 T	15-07-1996
		AU 671598 B	05-09-1996
		AU 2508592 A	16-03-1993
		BR 9206386 A	13-12-1994
		CA 2115155 A	04-03-1993
		CN 1070334 A	31-03-1993

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 98/08285

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9303705 A		CZ 9400351 A	18-05-1994
		DE 69211699 D	25-07-1996
		DE 69211699 T	28-11-1996
		DK 600013 T	28-10-1996
		EP 0600013 A	08-06-1994
		ES 2088590 T	16-08-1996
		FI 940770 A	18-02-1994
		GR 3020298 T	30-09-1996
		HU 67309 A	28-03-1995
		JP 6509808 T	02-11-1994
		MX 9204801 A	01-04-1993
		NO 940537 A	18-04-1994
		NZ 243995 A	28-08-1995
		PT 100790 A	30-09-1993
		SK 19394 A	09-11-1994

---





## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup> :</b> <b>A61K 7/00, C08F 291/00</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 98/51261</b> <b>(43) International Publication Date:</b> 19 November 1998 (19.11.98)
<b>(21) International Application Number:</b> PCT/IB98/00753 <b>(22) International Filing Date:</b> 18 May 1998 (18.05.98)  <b>(30) Priority Data:</b> 08/858,071      16 May 1997 (16.05.97)      US  <b>(71) Applicant:</b> THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US).  <b>(72) Inventors:</b> MIDHA, Sanjeev; Apartment 2D, 9274 Deercross Parkway, Blue Ash, OH 45236 (US). NIJAKOWSKI, Timothy, Roy; Apartment 15, 4003 Sharon Park Lane, Cincinnati, OH 45241 (US).  <b>(74) Agents:</b> REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217 (US).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the</i> <i>claims and to be republished in the event of the receipt of</i> <i>amendments.</i>
<b>(54) Title:</b> PERSONAL CARE COMPOSITIONS CONTAINING GRAFT POLYMERS		
<b>(57) Abstract</b> <p>Disclosed are personal care compositions comprising from about 0.1 % to about 15 % by weight of a graft polymer and from about 0.1 % to about 99.9 % by weight of a liquid carrier, wherein the graft polymer is made in accordance with the following process steps: (a) reacting copolymerizable monomers to form an organic polymeric backbone having a weight average molecular weight of from about 15,000 grams/mole to about 200,000 grams/mole and a plurality of organic halide moieties covalently bonded to and pendant from the polymeric backbone; and then (b) reacting copolymerizable monomers with the organic halide moieties of the polymeric backbone by atom transfer free radical polymerization in the presence of a catalytic amount of a Cu(I) salt or other transition metal species to form a plurality of polymeric side chains covalently bonded to and pendant from the polymeric backbone and having a weight average molecular weight of from about 500 grams/mole to about 200,000 grams/mole, wherein the polymeric backbone and the plurality of polymeric side chains form hydrophilic and hydrophobic graft polymers suitable for use in personal care compositions and having a weight average molecular weight of from about 16,000 grams/mole to about 10,000,000 grams/mole.</p>		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

## **PERSONAL CARE COMPOSITIONS CONTAINING GRAFT POLYMERS**

### **TECHNICAL FIELD**

The present invention relates to an improved method of making hydrophobic and hydrophilic graft polymers suitable for use in personal care compositions, and to hair styling compositions and other personal care compositions containing the graft polymers.

### **BACKGROUND OF THE INVENTION**

Personal care compositions such as hair sprays, styling shampoos, cosmetics, skin care products, and the like, often contain film-forming polymers for various reasons. These film-forming polymers are especially useful in hair care compositions to provide hair styling performance to the composition. Film-forming polymers for use in such compositions include organic or silicone-containing, linear or graft, copolymers which contain various monomers in an alternating, random, block or homopolymer configuration.

Graft copolymers are well known for use as film-forming polymers in hair care and other personal care compositions. These graft copolymers typically comprise a polymeric backbone and one or more macromonomers grafted to the backbone, wherein the physical and chemical attributes such as glass transition temperature values ( $T_g$ ), water solubility, and so forth are selected for the polymeric backbone and macromonomer grafts so as to provide the desired film-forming properties and other chemical or physical properties of the copolymers in a personal care composition. The graft copolymers are especially versatile in that the polymeric backbone and the attached macromonomer grafts can have select or different chemical or physical properties which collectively provide the optimal formulation or performance profile for the intended personal care composition in which it will be used.

Synthesis of graft copolymers, however, is typically more difficult than synthesis of many copolymers, especially linear polymers. Unlike linear polymer synthesis, the synthesis of graft copolymers typically involves a separate polymerization step involving the making of a macromonomer containing a reactive end group, copolymerization of the macromonomer with a copolymerizable,

ethylenically unsaturated monomer, and then termination of this last copolymerization step to obtain the desired graft polymers.

It has now been found that hydrophobic and hydrophilic graft polymers can now be made by simpler, more effective synthesis methods, and that these new synthesis methods result in the formation graft polymers which when applied to the hair or other surface form a polymeric film or weld having improved adhesive and cohesive strength. These polymers are very useful when used as film-forming polymers in personal care compositions, especially when used as film-forming or styling polymers in hair styling compositions. The graft polymers in these hair styling compositions provide improved styling and/or conditioning performance, and are especially effective in providing improved durability of hair style and improved hair feel.

It is therefore an object of the present invention to provide an improved method for making graft polymers, and further to provide such a method for making graft polymers for use in personal care compositions, and yet further to provide such a method which involves fewer synthesis steps than other conventional methods of making graft polymers. It is yet another object of the present invention to provide hair styling and other personal care compositions containing the graft polymers made in accordance with the synthesis method herein, wherein the graft polymers have a low polydispersity, and wherein the compositions contain low or reduced concentrations of polymer contaminants such as ungrafted polymeric backbone and/or unattached polymeric grafts or side chains.

### **SUMMARY OF THE INVENTION**

The present invention personal care compositions comprising from about from about 0.1% to about 15% by weight of a graft polymer and from about 0.1% to about 99.9% by weight of a liquid carrier, wherein the graft polymer is made in accordance with the process comprising the steps of (a) reacting copolymerizable monomers to form an organic polymeric backbone having a weight average molecular weight of from about 15,000 grams/mole to about 9,800,000 grams/mole and a plurality of organic halide moieties covalently bonded to and pendant from the polymeric backbone; and then (b) reacting copolymerizable monomers with the organic halide moieties of the polymeric backbone by atom transfer free radical polymerization in the presence of a catalytic amount of a transition metal species, preferably a Cu(I) salt and preferably complexed to a suitable ligand, to form a plurality of polymeric side chains covalently bonded to and pendant from the polymeric backbone and having a weight average molecular weight of from about



500 grams/mole to about 200,000 grams/mole, wherein the polymeric back bone and the plurality of polymeric side chains form graft polymers suitable for use in personal care compositions and having a weight average molecular weight of from about 16,000 grams/mole to about 10,000,000 grams/mole.

It has been found that the above-described process limitations allow for a simpler, more effective, synthesis of graft polymers using fewer process steps than conventional synthesis methods, and also allows for the synthesis of graft polymers without reliance upon the use of copolymerizable macromonomers, or a separate synthesis step for making such macromonomers. It has also been found that personal care compositions containing these graft polymers contain low or reduced concentrations of polymer contaminants such as ungrafted polymeric backbone and/or unattached polymeric grafts or side chains, wherein the graft polymers also have a low or reduced polydispersity.

#### **DETAILED DESCRIPTION OF THE INVENTION**

The process limitations of present invention comprise two key reactions steps. In a first reaction step, copolymerizable monomers are reacted together to form a polymeric backbone containing organic halide moieties covalently bonded to and pendant from the backbone. In a second subsequent reaction step, the polymeric backbone is reacted with copolymerizable monomers by atom transfer radical polymerization in the presence of a catalytic amount of a Cu(I) salt or other transition metal species, preferably complexed to a suitable ligand. Each of these two essential process steps are described in detail hereinafter.

The terms "hydrophilic" or "water soluble" as used herein, unless otherwise specified, are used interchangeably and refer to polymers (or salt forms of such polymers produced by neutralization or quaternization of acidic or basic groups) or other materials that are soluble in distilled water, ethanol, *n*-propanol, isopropanol, or combinations thereof, at 25°C and at a concentration of 0.2% by weight of such polymer or other material. The terms "hydrophobic" and "water insoluble" as used herein, unless otherwise specified, are used interchangeably and refer to all other polymers or materials that are not hydrophilic as defined herein.

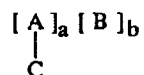
The method of the present invention can comprise, consist of, or consist essentially of the essential elements or limitations of the invention described herein, as well as any of the additional or optional elements or limitations described herein.

All molecular weights as used herein, unless otherwise specified, are weight average molecular weights expressed as grams/mole.

All percentages, parts and ratios are by weight of the total referenced composition, unless otherwise specified. All such weights as they pertain to listed ingredients are based on the active level and, therefore, do not include solvents or by-products that may be included in commercially available materials, unless otherwise specified.

### **Synthesis Method**

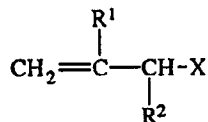
The personal care compositions of the present invention comprise graft polymers made in accordance with the process limitations herein, which process comprises two essential reaction steps. In the first reaction step, the polymeric backbone of the graft polymers herein are first prepared. This is accomplished by reacting copolymerizable monomers to form a polymeric backbone containing a plurality of organic halide moieties covalently bonded to and pendant from the polymeric backbone, and includes those polymers which conform generally to the formula



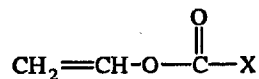
where "A" is a monomer unit having an organic halide moiety "C" attached which is covalently bonded to and pendant from the "A" monomer unit, and "B" is a monomer unit that is copolymerizable with the "A" monomer unit, "a" is a positive integer having a value of 2 or greater, preferably a value of from about 2 to about 30; and "b" is a positive integer having a value of at least about 4, preferably a value of from about 10 to about 2000. The organic halide moiety "C" includes any linear, branched or cyclic (aromatic or otherwise) carbon structure, whether substituted or unsubstituted, which also contain a halogen atom (F, Cl, Br or I).

In the first reaction step of the synthesis method herein, the "A" monomer unit with the attached organic halide moiety "C" is preferably selected from the group of allyl monomers, vinyl acetate monomers, acid halide monomers, styryl monomers, or combination thereof, and more preferably selected from the monomer units characterized by the following general structures (Groups I-V):

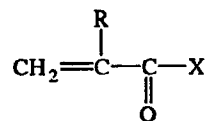
(I)



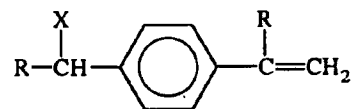
(II)



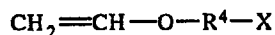
(III)



(IV)



(V)



where R is methyl or hydrogen; X is a halogen atom (F, Cl, Br, I); R<sup>1</sup> and R<sup>2</sup> are each independently selected from methyl, hydrogen or methoxy; and R<sup>4</sup> is an alkyl group having from 1 to 8 carbon atoms.

The first reaction step of the process herein involves any conventional or otherwise known polymerization techniques such as ionic, Ziegler-Natta, free radical, group transfer or step growth polymerization, or combinations thereof. The first reaction step preferably involves conventional free radical polymerization techniques. Once the first reaction is complete, or has progressed to the extent desired, the first reaction step is terminated or allowed to terminate depending on the polymerization method selected, the degree or extent of polymerization desired, the reactivity of the monomer units selected for use in the reaction, and so forth. Any conventional or otherwise known termination technique appropriate for the selected reaction and reaction conditions may be used. For example, and most typically, after polymerization of the polymeric backbone by free radical polymerization, the

reaction mixture is heated to about 120°C for about 15 minutes to consume or react any remaining free radical initiator, and thereafter the reaction mixture is cooled or allowed to cool to room temperature to allow the reaction to self terminate before addition of ingredients to start the second reaction step.

In the second reaction step of the process of the present invention, the polymeric backbone described hereinabove is reacted with one or more copolymerizable monomers in the presence of a catalytic amount of a transition metal salt, preferably a Cu(I) salt and preferably complexed to a suitable ligand. In this reaction step, the organic halide moieties act as initiators in the presence of the copolymerizable monomers and the catalyst, resulting in the grafting of the monomers onto the polymeric backbone by atom transfer free radical polymerization, the monomers forming a plurality of polymeric side chains covalently bonded to and pendant from the backbone. The polymeric side chains form on the polymeric backbone without the need to use copolymerizable macromonomers to achieve the pendant polymeric graft chains.

The catalyst for the second reaction step is a transition metal salt, preferably a Cu(I) salt such as Cu(I) halide salts (Cl, F, Br, I) and which is preferably complexed to a ligand which is suitable for solubilizing the Cu(I) salt in the reaction mixture, wherein the reaction mixture of the second reaction step comprises dissolved or partially dissolved polymer, unreacted monomer, solvent and catalyst. Preferred ligands for use in solubilizing the Cu(I) salts in the reaction mixture are aprotic bidentates such as diphosphates, 2,2' bipyridyl, C1-C20 alkyl substituted bipyridyl and combinations thereof. Most preferred is 2,2' bipyridyl complexed to a Cu(I) halide salt, especially Cu(I) Cl. Other conventional or otherwise known ligands can be used herein provided that they do not substantially and unduly impair the polymerization reaction of the process herein, some examples of which are described in "The Use of Living Radical Polymerization to Synthesize Graft Copolymers" Dept. of Chemistry, Carnegie Mellon University, Pittsburgh, Pennsylvania; Simion Cocoa and Krzysztof Matyjaszewski, Polymer Preprints, Vol. 37(1), pg. 571-572, 1996. "Alternating Copolymers of Methyl Acrylate with Isobutene and Isobutyl Vinyl Ether using ATRP" Dept. of Chemistry, Carnegie Mellon University, Pittsburgh, Pennsylvania; Timothy e. Patten et al. Polymer Preprints, Vol. 37(1), pg. 573-574, 1996., "Radical Polymerization yielding Polymers with Mw/Mn ~1.05 by Homogeneous Atom Transfer Radical Polymerization" Carnegie Mellon University, Pittsburgh, Pennsylvania; T.E. Patten et al. Polymer Preprints, Vol. 37(1), pg. 575-576, 1996. "The Synthesis of End Functional Polymers by Living Radical Polymerization" Carnegie Mellon University, Pittsburgh, Pennsylvania, Y. Nakagawa

et al., Polymer Preprints, Vol. 37(1), pg. 577-578, 1996, which publications are incorporated herein by reference.

### Graft Polymers

The process limitations of the present invention are especially useful for making hydrophobic or hydrophilic, film-forming polymers suitable for use in personal care compositions such as hair styling compositions. Graft polymers made in accordance with these process limitations typically have a low or reduced polydispersity and contain reduced concentrations of polymer contaminants such as ungrafted polymeric backbone and/or unattached polymeric grafts or side chains once the two step reaction steps of the synthesis are complete.

Graft polymers made in accordance with the synthesis method herein are characterized by a hydrophilic or hydrophobic polymeric backbone with a plurality of hydrophobic or hydrophilic polymeric side chains covalently bonded to and pendant from the polymeric backbone, wherein the polymeric backbone represents from about 50% to about 99%, preferably from about 60% to about 98%, more preferably from about 75% to about 95%, by weight of the graft polymer, and the plurality of polymeric side chains represent from about 1% to about 50%, preferably from about 2% to about 40%, more preferably from about 5% to about 25%, by weight of the graft polymer.

The polymeric side chains on the graft polymers have a weight average molecular weight of at least about 500 grams/mole, preferably from about 1,000 grams/mole to about 200,000 grams/mole, more preferably from about 1,500 grams/mole to about 30,000 grams/mole, most preferably from about 3,000 grams/mole to about 25,000 grams/mole. These polymeric side chains may comprise monomer units arranged in an alternating, random, block or homopolymer configuration, and each of the polymeric side chains may comprise the same or different monomers, arranged in the same or different configuration.

The graft polymers made in accordance with the synthesis method herein have a weight average molecular weight of from about 16,000 grams/mole to about 10,000,000 grams/mole, preferably less than about 5,000,000 grams/mole, more preferably less than about 3,000,000. Most preferred are weight average molecular weights of from about 50,000 grams/mole to about 2,000,000 grams/mole, more preferably from about 75,000 grams/mole to about 1,000,000 grams/mole, and even more preferably from about 75,000 grams/mole to about 750,000 grams/mole.

The graft polymers made in accordance with the synthesis method herein can have a single Tg value and preferably are copolymers having at least two distinct

immiscible phases, wherein the polymeric side chains are closely associated with each other and exist in one phase and the polymeric backbone of the copolymer remains in a second separate phase. A consequence of this phase immiscibility is that if the temperature separation between each of the Tg values involved is large enough then these copolymers exhibit two distinct glass transition temperatures, namely one Tg value for the backbone and one Tg value for the side chain. The copolymers can also exhibit a third glass transition temperature corresponding to any optional polysiloxane side chains on the graft copolymers. Whether such a third Tg value is observable depends upon a number of factors including the percent silicone in the copolymer, the number of polysiloxane side chains in the copolymer, the temperature separation between each of the Tg values involved, and other such physical factors.

The graft polymers made in accordance with synthesis method herein also preferably have a polydispersity of less than about 10, preferably less than about 5, even more preferably less than about 4.

Monomers suitable for use in the synthetic method herein can be hydrophilic or hydrophobic. In this context, the term "hydrophobic monomers" are those copolymerizable monomers which when reacted together form hydrophobic or water insoluble homopolymers, and the term "hydrophilic monomers" refers to those copolymerizable monomers which when reacted together form hydrophilic or water soluble homopolymers.

Monomers suitable for use herein must be copolymerizable and have the requisite characteristics defined herein for use in the synthetic method. These copolymerizable monomers are preferably ethylenically unsaturated monomers, more preferably copolymerizable vinyl monomers. The term "copolymerizable" as used herein means that a material can be reacted with another material in accordance with the first and/or second polymerization reaction steps of the synthesis method herein, whichever is appropriate. The term "ethylenically unsaturated" as used herein refers to monomers that contain at least one polymerizable carbon-carbon double bond (which can be mono-, di-, tri-, or tetra-substituted).

Such copolymerizable monomers include the copolymerizable organic halide-containing monomers described hereinbefore, and also includes the monomer units that are reacted with the organic halide-containing monomers in the first reaction step of the synthesis method, and also includes the monomer units that are reacted with the polymeric backbone in the second reaction step of the synthesis method.

Copolymerizable monomers for use in the first and second reaction steps of the synthesis method may be the same, or may include combinations of two or more different but copolymerizable monomers, including combinations of hydrophilic and

hydrophobic monomers, combinations of copolymerizable monomers having different but select glass transition temperatures ( $T_g$ ), combinations of polar and nonpolar monomers, and so forth, or combinations of two or more copolymerizable monomers from a single chemical class or otherwise having similar physical or chemical characteristics. The graft polymers may therefore comprise the same or different monomer units, and may therefore be classified as homopolymers, copolymers, terpolymers and so forth.

Nonlimiting classes of monomers useful herein include monomers selected from the group consisting of unsaturated alcohols, unsaturated monocarboxylic acids, unsaturated dicarboxylic acids, unsaturated anhydrides, alcohol esters of unsaturated monocarboxylic acids, alcohol esters of unsaturated dicarboxylic acids, alcohol esters of unsaturated anhydrides, alkoxylated esters of unsaturated monocarboxylic acids, alkoxylated esters of unsaturated dicarboxylic acids, alkoxylated esters of unsaturated anhydrides, aminoalkyl esters of unsaturated monocarboxylic acids, aminoalkyl esters of unsaturated dicarboxylic acids, aminoalkyl esters of unsaturated anhydrides, amides of unsaturated monocarboxylic acids, amides of unsaturated dicarboxylic acids, amides of unsaturated anhydrides, salts of unsaturated monocarboxylic acids, salts of unsaturated dicarboxylic acids, salts of unsaturated anhydrides, unsaturated hydrocarbons, unsaturated heterocycles, and mixtures thereof.

Representative examples of such monomers include acrylic acid (produced by hydrolysis of trimethylsilyl acrylate), methacrylic acid (produced by hydrolysis of trimethylsilyl methacrylate), trimethylsilyl acrylate, trimethylsilyl methacrylate, acrylamide, acrylate alcohols produced by hydrolysis of trimethylsilyl protected alcohol, hydroxyethyl methacrylate, diallyldimethyl ammonium chloride, vinyl pyrrolidone, vinyl ethers (such as methyl vinyl ether), maleimides, vinyl pyridine, vinyl imidazole, other polar vinyl heterocyclics, styrene sulfonate, allyl alcohol, vinyl alcohol (such as that produced by the hydrolysis of vinyl acetate after polymerization), vinyl caprolactam, methacrylic acid esters of  $C_1$ - $C_{18}$  alcohols, such as methanol, ethanol, methoxy ethanol, 1-propanol, 2-propanol, 1-butanol, 2-methyl-1-propanol, 1-pentanol, 2-pentanol, 3-pentanol, 2-methyl-1-butanol, 1-methyl-1-butanol, 3-methyl-1-butanol, 1-methyl-1-pentanol, 2-methyl-1-pentanol, 3-methyl-1-pentanol, t-butanol(2-methyl-2-propanol), cyclohexanol, neodecanol, 2-ethyl-1-butanol, 3-heptanol, benzyl alcohol, 2-octanol, 6-methyl-1-heptanol, 2-ethyl-1-hexanol, 3,5-dimethyl-1-hexanol, 3,5,5-trimethyl-1-hexanol, 1-decanol, 1-dodecanol, 1-hexadecanol, 1-octadecanol, and the like, the alcohols having from about 1-18 carbon atoms with the number of carbon atoms preferably being from about 1-12; dicyclopentenyl acrylate; 4-biphenyl acrylate; pentachlorophenyl acrylate; 3,5-

dimethyladamantyl acrylate; 3,5-dimethyladamentyl methacrylate; 4-methoxycarbonylphenyl methacrylate; trimethylsilyl acrylate, trimethylsilyl methacrylate; styrene; alkyl substituted styrenes including alpha-methylstyrene and t-butylstyrene; vinyl esters, including vinyl acetate, vinyl neononanoate, vinyl pivalate and vinyl propionate; vinyl chloride; vinylidene chloride; vinyl toluene; alkyl vinyl ethers, including isobutyl vinyl ether and s-butyl vinyl ether; butadiene; cyclohexadiene; bicycloheptadiene; 2,3-dicarboxymethyl-1,6-hexadiene; ethylene; propylene; indene; norbornylene;  $\beta$ -pinene;  $\alpha$ -pinene; salts of acids and amines listed above, and combinations thereof. The quaternized monomers can be quaternized either before or after the copolymerization with other monomers of the graft copolymer.

Preferred monomers include acrylic acid (produced by hydrolysis of trimethylsilyl acrylate), methacrylic acid (produced by hydrolysis of trimethylsilyl methacrylate), vinyl pyrrolidone, acrylic or methacrylic acid esters of C<sub>1</sub>-C<sub>18</sub> alcohols, trimethylsilyl acrylate, trimethylsilyl methacrylate, styrene, alpha-methylstyrene, t-butylstyrene, vinyl acetate, vinyl propionate, 2-methoxyethyl acrylate, 2-ethoxyethyl acrylate, n-butyl methacrylate, isobutyl methacrylate, t-butyl acrylate, t-butyl methacrylate, 2-ethylhexyl methacrylate, methyl methacrylate, and mixtures thereof.

The suitable copolymerizable monomers described herein are meant to include those corresponding copolymerizable monomers that are unsubstituted or substituted with one or more substituent groups, provided that such groups do not unduly impair the polymerization reactions of the synthesis method. Examples of suitable substituent groups include, but are not limited to, alkyl, aryl, carboxyl, halo groups, and combinations thereof.

Specific examples of hydrophilic graft polymers made in accordance with the process limitations of the present invention include, but are not limited to,

Poly(2-methoxyethyl acrylate-co-methacrylic acid-co-tert-butyl acrylate-co-4-chloromethyl styrene)-graft-poly(styrene-co-methacrylic acid); molecular weight of 150,000 grams/mole, Composition : 2-methoxyethyl acrylate (31.6%), methacrylic acid (22%), tert-butyl acrylate (28%) 4-chloromethyl styrene (0.4%), styrene (18%)



Poly(2-methoxyethyl acrylate-co-methacrylic acid-co-tert-butyl acrylate-co-4-chloromethyl styrene)-graft-[poly(styrene-co-methacrylic acid);poly(dimethylsiloxane)]; molecular weight of 150,000 grams/mole, Composition : 2-methoxyethyl acrylate (26.6%), methacrylic acid (22%), tert-butyl acrylate (28%) 4-chloromethyl styrene (0.4%), poly(dimethylsiloxane) macromonomer (molecular weight 10,000 grams/mole) (5%) styrene (18%).

Poly(t-butyl acrylate-co-2-methoxyethyl acrylate-co-acrylic acid-co-4-chloromethyl styrene)-graft-poly(iso-butyl methacrylate-co-methacrylic acid); molecular weight 80,000 grams/mole; Composition : t-butyl acrylate (22%), 2-methoxyethyl acrylate (31%), acrylic acid (18%), 4-chloromethyl styrene (1%), isobutyl methacrylate (15%), methacrylic acid (13%)

Poly(vinyl acetate-co-vinyl pyrrolidone-co-chlorovinyl acetate)-graft-poly(styrene-co-methacrylic acid); molecular weight 120,000 grams/mole; Composition : vinyl acetate (40%), vinyl pyrrolidone (39%), chlorovinyl acetate (1%), isobutyl methacrylate (10%), dimethylaminoethyl methacrylate (10%).

The hydrophilic graft polymers made in accordance with the synthesis methods herein may comprise acidic functionalities, such as carboxyl groups, and are usually used in at least partially neutralized form to promote solubility or dispersability of the polymer. In addition, use of the neutralized form aids in the ability of the hair styling compositions to be removed from the hair by shampooing. The extent of such neutralization ranges from about 10% to 100%, more preferably from about 20% to about 90%, even more preferably from about 40% to about 85%, neutralization of the acidic functionalities of the graft polymer.

Neutralization of the hydrophilic graft polymers containing acidic functionalities may be accomplished by any conventional or otherwise known technique for affecting such neutralization by using an organic or inorganic base material. Metallic bases are particularly useful for this purpose. Suitable base neutralizers include, but are not limited to, ammonium hydroxides, alkali metal hydroxides, or an alkaline earth metal hydroxides, preferably potassium hydroxide and sodium hydroxide. Examples of other suitable neutralizing agents include, but are not limited to, amines or amino alcohols such as 2-amino-2-methyl-1,3-propanediol (AMPD), 2-amino-2-ethyl-1,3-propanediol (AEPD), 2-amino-2-methyl-1-propanol (AMP), 2-amino-1-butanol (AB), monoethanolamine (MEA),

diethanolamine (DEA), triethanolamine (TEA), monoisopropanolamine (MIPA), diisopropanolamine (DIPA), triisopropanolamine (TIPA) and dimethyl stearamine (DMS) and combinations thereof. Preferred are amines and metallic bases.

Neutralization of hydrophilic polymers containing basic functionalities, e.g., amino groups, are likewise preferably at least partially neutralized with an organic or inorganic acid e.g., hydrogen chloride. Neutralization can be accomplished by any conventional or otherwise known technique for accomplishing such neutralization. The preferred extent of neutralization is the same as that described for neutralization of acidic functionalities. Solubility for any neutralized graft polymer made in accordance with the synthesis method herein should be determined only after the desired acid or base neutralization.

Specific examples of hydrophobic graft polymers made in accordance with the process limitations of the present invention include, but are not limited to,

Poly(tert-butyl acrylate-co-2-ethylhexyl methacrylate-co-chloromethyl styrene)-graft-poly(n-butyl acrylate); molecular weight 100,000 grams/mole;  
Composition; tert-butyl acrylate(54%), 2-ethylhexyl methacrylate (10%), 4-chloromethyl styrene (6%); n-butyl acrylate(30%)

Poly(t-butyl acrylate-co-2-methoxyethyl acrylate-co-4-chloromethyl styrene)-graft-poly(styrene); molecular weight 100,000 grams/mole;  
Composition : t-butyl acrylate (25%), 2-methoxyethyl acrylate (50%), 4-chloromethyl styrene (2%); styrene(23%)

Poly(vinyl acetate-co-vinyl pyrrolidone-co-chlorovinyl acetate)-graft-poly(2-ethylhexyl acrylate); molecular weight 120,000 grams/mole;  
Composition : vinyl acetate (40%), vinyl pyrrolidone (10%), chlorovinyl acetate (5%),  
2- ethylhexyl acrylate.(45%)

#### **Optional Silicone Grafts**

The process limitations of the present invention may further comprise the copolymerization of silicone macromonomers with other copolymerizable monomers described herein during the first reaction step of the synthesis method of the present invention, to thus form a polymeric backbone comprising one or more silicone-grafted side chains and a plurality of organic halide moieties attached to and pendent from the polymeric backbone. The resulting silicone grafted polymeric backbone is

then subjected to the second reaction step of the process as described hereinbefore, thus producing graft copolymers comprising a plurality of nonsilicone-containing polymeric side chains in combination with one or more silicone-containing macromonomer grafts.

The optional silicone macromonomer is grafted to or polymerized into the polymeric backbone by any conventional or otherwise known method for making silicone graft copolymers. Most typically, these polymers are formed from the random copolymerization of vinyl or otherwise copolymerizable monomer units, some or all of which have attached organic halide moieties, and polysiloxane-containing macromonomer units containing a polymeric portion and a vinyl moiety copolymerizable with monomer units. Upon completion of polymerization, the siloxane polymeric portion of the macromonomer unit forms the polysiloxane side chains of the graft copolymer. The other copolymerizable monomer units and the vinyl portion of the macromonomer units form the polymeric backbone. The copolymerizable monomer and the polysiloxane-containing macromonomer can be selected from a wide variety of structures as long as the copolymer has the required properties described herein, including having the attached organic halide moieties which act as initiators in the second reaction step of the synthesis method herein.

Examples of related silicone graft copolymers, and methods of making them, are described in detail in U.S. Patent 4,693,935, Mazurek, issued September 15, 1987, U.S. Patent 4,728,571, Clemens et al., issued March 1, 1988, both of which are incorporated herein by reference. Additional silicone grafted polymers are also disclosed in EPO Application 90307528.1, published as EPO Application 0 408 311 A2 on January 11, 1991, Hayama, et al., U.S. Patent 5,061,481, issued October 29, 1991, Suzuki et al., U.S. Patent 5,106,609, Bolich et al., issued April 21, 1992, U.S. Patent 5,100,658, Bolich et al., issued March 31, 1992, U.S. Patent 5,100,657, Ansher-Jackson, et al., issued March 31, 1992, U.S. Patent 5,104,646, Bolich et al., issued April 14, 1992, U.S. Serial No. 07/758,319, Bolich et al, filed August 27, 1991, and U.S. Serial No. 07/758,320, Torgerson et al., filed August 27, 1991, which descriptions are incorporated herein by reference.

The silicone graft copolymers made in accordance with the synthesis methods herein may comprise from zero to about 50%, preferably from about 2% to about 40%, and more preferably from about 10% to about 30%, polysiloxane macromonomer units by weight of the graft polymer.

The polysiloxane macromonomer units are copolymerizable with the other selected monomers for use in the first reaction step of the synthesis method, the polysiloxane macromonomers having a vinyl or other copolymerizable moiety for

reaction with the other selected monomer. Either a single type of polysiloxane macromonomer unit or combinations of two or more polysiloxane macromonomer units can be used in the first reaction step. In this context, the term "copolymerizable" means that the polysiloxane macromonomers can be reacted with the other selected monomers, including the organic halide-containing monomers, in accordance with the first reaction step of the synthesis method herein, which results in the requisite polymeric backbone for use in the second reaction step of the synthesis method herein.

The polysiloxane macromonomers that are useful herein contain a polymeric portion and a copolymerizable moiety which is preferably an ethylenically unsaturated moiety. Typically, the preferred macromonomers are those that are endcapped with the vinyl moiety. By "endcapped" as used herein is meant that the vinyl moiety is at or near a terminal position of the macromonomer.

The polysiloxane macromonomers can be synthesized using a variety of conventional or otherwise known synthetic techniques familiar to the polymer chemist of ordinary skill in the art. Furthermore, these polysiloxane macromonomers can be synthesized starting from commercially available polymers. Typically, the weight average molecular weight of the polysiloxane macromonomer for use in the first reaction step is from about 1,000 grams/mole to about 50,000 grams/mole.

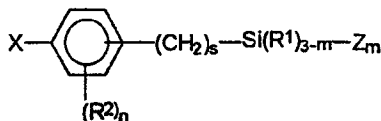
Polysiloxane macromonomers suitable for use herein include those which conform to the general formula:



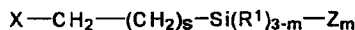
wherein X is a vinyl group copolymerizable with the vinyl monomer units; Y is a divalent linking group; each R is independently selected from the group consisting of hydrogen, hydroxyl, C1-C6 alkyl, C1-C6 alkoxy, C2-C6 alkylamino, styryl, phenyl, C1-C6 alkyl or alkoxy-substituted phenyl; Z is a monovalent siloxane polymeric moiety having a number average molecular weight of at least about 1000 and which is essentially unreactive under copolymerization conditions; n is an integer having a value of 0 or 1; and m is an integer having a value of from 1 to 3. The polysiloxane macromonomer has a weight average molecular weight from about 1,000 grams/mole to about 50,000 grams/mole, preferably from about 5,000 grams/mole to about 30,000 grams/mole, more preferably from about 8,000 grams/mole to about 25,000 grams/mole.

Preferably, the polysiloxane macromonomer has a formula selected from the following formulas I-III

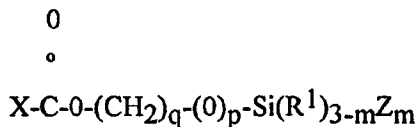
(I)



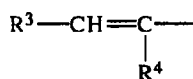
(II)



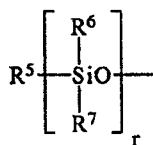
(III)



wherein *s* is an integer having a value of from 0 to 6; preferably 0, 1, or 2; more preferably 0 or 1; *m* is an integer having a value of from 1 to 3, preferably 1; *p* is an integer having a value of 0 or 1; *q* is an integer having a value of from 2 to 6; each R<sup>1</sup> is independently selected from the group consisting of hydrogen, hydroxyl, C1-C6 alkyl, C1-C6 alkoxy, C2-C6 alkylamino, phenyl, C1-C6 alkyl or alkoxy-substituted phenyl, preferably C1-C6 alkyl, or C1-C6 alkyl or alkoxy-substituted phenyl, more preferably C1-C6 alkyl, even more preferably methyl, R<sup>2</sup> is selected from the group consisting of C1-C6 alkyl or C1-C6 alkyl substituted phenyl, preferably methyl; *n* is an integer having a value of from 0 to 4, preferably 0 or 1, more preferably 0; X is



wherein R<sup>3</sup> is hydrogen or -COOH, preferably R<sup>3</sup> is hydrogen; R<sup>4</sup> is hydrogen, methyl or -CH<sub>2</sub>COOH, preferably R<sup>4</sup> is methyl; Z is



wherein R<sup>5</sup>, R<sup>6</sup>, and R<sup>7</sup>, are independently selected from hydrogen, hydroxyl, C1-C6 alkyl, C1-C6 alkoxy, C2-C6 alkylamino, styryl, phenyl, C1-C6 alkyl or alkoxy-substituted phenyl, hydrogen or hydroxyl, preferably R<sup>5</sup>, R<sup>6</sup>, and R<sup>7</sup> are C1-C6 alkyls; more preferably methyl; and *r* is an integer having a value of from about 14 to

about 700, preferably about 60 to about 400, and more preferably about 100 to about 170.

### **Personal Care Compositions**

The graft polymers made in accordance with the methods herein are especially useful when used as film-forming polymers in personal care compositions. Such compositions comprise the graft polymers made in accordance with the methods herein in combination with a suitable liquid carrier to dissolve or disperse, preferably dissolve, the graft polymer in the personal care composition.

The personal care compositions of the present invention include skin care compositions, styling or conditioning shampoo compositions, cosmetic compositions, or other similar compositions, many of which will further comprise one or more optional ingredients as described hereinafter. Preferred are hair care compositions such as conditioners, styling and/or conditioning shampoos, hair sprays, and styling mousses, tonics, gels or lotions. The film-forming graft polymer for use in such compositions, and which is made in accordance with the synthesis methods herein, provides the compositions with hair or skin conditioning performance or hair styling performance. The personal care compositions can be formulated as solids or liquids, single or multi-phase systems, emulsions, dispersions, solutions, gels, suspensions, or other formulation suitable for application to the skin or hair.

The personal care compositions of the present invention comprise the graft polymers made in accordance with the methods herein, at concentrations effective to provide the desired film-forming properties. Such concentrations generally range from about 0.1% to about 15%, preferably from about 0.5% to about 15%, even more preferably from about 0.5% to about 8%, even more preferably from about 1% to about 8%, by weight of the personal care composition, wherein the concentration of the liquid carrier generally ranges from about 85% to about 99.9%, preferably from about 92% to about 99.5%, even more preferably from about 92% to about 99%, by weight of the personal care composition.

The personal care compositions, especially when formulated as hair styling compositions, may be dispensed as sprayed or atomized liquids from pump spray or aerosol canisters. The aerosolized compositions comprise one or more conventional or otherwise known aerosol propellants. Suitable propellants include any liquifiable gas known or otherwise effective for use in this manner, examples of which include volatile hydrocarbon propellants such as liquified lower hydrocarbons having 3 or 4 carbon atoms such as propane, butane, isobutane, or combinations thereof. Other suitable propellants include hydrofluorocarbons such as 1,2-difluoroethane, and other

propellants such as dimethylether, nitrogen, carbon dioxide, nitrous oxide, atmospheric gas, and combinations thereof. Preferred are hydrocarbon propellants, particularly isobutane when used alone or in combination with other hydrocarbon propellants. Propellant concentrations should be sufficient to provide the desired delivery or application of the personal care composition to the hair or skin, which concentrations typically range from about 10% to about 60%, preferably from about 15% to about 50%, by weight of the composition.

Pressurized aerosol dispensers can also be used where the propellant is separated from contact with the hair styling composition, an example of which would be a two compartment canister available from the American National Can Corp. under the trade name SEPRO. Other suitable aerosol dispensers are those characterized by the propellant being compressed air which can be filled into the dispenser by means of a pump or equivalent device prior to use. Such dispensers are described in U.S. Patent 4,077,441, U.S. Patent 4,077,441 and U.S. Serial No. 07/839,648, which descriptions are incorporated herein by reference. Conventional non-aerosol pump spray dispensers or atomizers are also suitable for use herein.

#### A) Hydrophilic graft polymer compositions

The personal care compositions of the present invention preferably comprise a hydrophilic graft polymer made in accordance with the synthesis methods herein, and which is used in combination with a hydrophilic or water soluble or miscible liquid carrier suitable for solubilizing or dispersing the hydrophilic graft polymer in the personal care composition. These preferred compositions are especially useful when used as hair spray or other hair styling compositions.

Hydrophilic liquid carriers suitable for use herein include, but are not limited to, water, ethanol, *n*-propanol, isopropanol, and combinations thereof, preferably a combination of an alcohol and water wherein the water content of the composition ranges from about 0.5% to about 99%, preferably from about 0.5% to about 50%, by weight of the composition, and the alcohol content ranges from about 0.5% to about 99%, preferably from about 50% to about 95%, by weight of the composition.

The hydrophilic graft polymers preferably have at least two distinct glass transition temperatures ( $T_g$ ), the first of which is associated with the polymeric backbone and the second of which is associated with the plurality of polymeric side chains attached thereto. The polymeric backbone preferably has a  $T_g$  value of less than about 35 °C, more preferably less than about 25°C, even more preferably less than about 10°C, wherein the plurality of polymeric side chains have a  $T_g$  value

preferably greater than about 50°C, more preferably greater than about 60 °C, even more preferably greater than about 70°C.

Other suitable hydrophilic graft polymers made in accordance with the methods herein include those having a Tg value for the polymeric backbone of greater than about 30 °C, more preferably greater than about 40°C, even more preferably greater than about 50°C, wherein the plurality of polymeric side chains have a Tg value preferably of less than about 10°C, more preferably less than about 0 °C, even more preferably less than about -20°C.

These personal care compositions, especially when formulated as hair spray compositions, preferably contain reduced concentrations of volatile organic compounds, including volatile organic solvents. In this context, the volatile organic compounds or solvents are those organic compounds or solvents that contain less than 12 carbon atoms or have a vapor pressure greater than 0.1mm of mercury. Water concentrations in these preferred compositions are typically at least about 10% by weight of the composition, preferably from about 10% to about 50% by weight of the composition, wherein the concentration of the volatile organic compound or solvent is typically less than about 90%, preferably from about 20% to about 80%, more preferably from about 40% to about 70%, even more preferably from about 40% to about 60%, by weight of the composition.

#### B) Hydrophobic graft polymer compositions

Another embodiment of the personal care compositions of the present invention are those which comprise a hydrophobic graft polymer made in accordance with the synthesis methods herein, in combination with a hydrophobic or water insoluble liquid carrier suitable for solubilizing or dispersing or otherwise carrying the hydrophobic graft polymer in the personal care composition. These embodiments are especially useful when used as hair or skin conditioning compositions, some nonlimiting examples of which include skin care compositions, conditioning shampoos, and hair conditioners.

Suitable hydrophobic liquid carriers for the hydrophobic graft polymers include hydrophobic, volatile, liquids such as volatile branched chain hydrocarbons, silicones and combinations thereof. The concentration of such liquid carriers in the composition preferably range from about 0.1% to about 75%, more preferably from about 0.2% to about 25%, and even more preferably from about 0.5% to about 15%, by weight of the composition, wherein the weight ratio of hydrophobic graft polymer to the hydrophobic liquid carrier is generally from about 1:100 to about 5:1,



preferably from about 1:10 to about 1:1, more preferably from about 1:8 to about 2:3.

The hydrophobic liquid carrier is preferably a volatile liquid which exhibits a significant vapor pressure at ambient conditions (e.g., 1 atmosphere, 25°C). In this context, the term "volatile" refers to solvents or liquid carriers having a boiling point at one atmosphere of 260°C or less, preferably 250°C or less, more preferably 230°C or less, most preferably 225°C or less. In addition, the boiling point of the hydrophobic liquid carrier will generally be at least about 50°C, preferably at least about 100°C. The term "nonvolatile" as used in this context refers to solvents or liquid carriers which have a boiling point at one atmosphere of greater than 260°C.

The hydrophobic graft polymer is preferably soluble in the selected hydrophobic liquid carrier. In this context, the term "soluble" refers to the solubility of the hydrophobic graft polymer in the hydrophobic liquid carrier at 25°C at a concentration of 0.1%, preferably at 1%, more preferably at 5%, most preferably at 15%, by weight of the hydrophobic liquid carrier.

Preferred hydrophobic liquid carriers include hydrophobic, volatile, branched chain hydrocarbons, preferably saturated hydrocarbons, which contain from about 10 to about 16, preferably from about 12 to about 16, most preferably from about 12 to about 14, carbon atoms. Examples of such preferred branched chain hydrocarbons include isoparaffins of the above chain sizes. Isoparaffins are commercially available from Exxon Chemical Co.; examples include Isopar™ H and K (C<sub>11</sub>-C<sub>12</sub> isoparaffins), and Isopar™ L (C<sub>11</sub>-C<sub>13</sub> isoparaffins). Other suitable branched chain hydrocarbons are isododecane and isohexadecane. Isododecane is preferred and is commercially available from Preperse, Inc. (South Plainfield, NJ, USA) as Permethyl™ 99A.

Preferred hydrophobic silicone carriers include hydrophobic, volatile siloxanes (such as phenyl pentamethyl disiloxane, phenylethyl pentamethyl disiloxane, hexamethyl disiloxane, methoxypropyl heptamethyl cyclotetrasiloxane, chloropropyl pentamethyl disiloxane, hydroxypropyl pentamethyl disiloxane, cyclomethicones, including octamethyl cyclotetrasiloxane and decamethyl cyclopentasiloxane), and mixtures thereof. Preferred hydrophobic silicone solvents are cyclomethicones, more preferably octamethyl cyclotetrasiloxane and decamethyl cyclopentasiloxane.

It is understood that the hydrophobic liquid carriers can be used in combination with the hydrophilic liquid carriers in the personal care compositions, and that the hydrophobic graft polymers can likewise be used in combination with the hydrophilic graft polymers in the personal care composition. Such combinations are suitable for use in the personal care composition provided that they are physically and

chemically compatible with the selected ingredients in the composition, and do not otherwise substantially and unduly impair product performance.

### **Optional Ingredients**

The personal care compositions described herein may further comprise one or more optional ingredients known or otherwise effective for use in hair styling compositions or other personal care compositions. These optional ingredients may be used to improve or otherwise modify aesthetics, performance or stability of the hair styling compositions. Concentrations of such optional ingredients will vary with the type of material added and its intended performance, but will typically and collectively range from about 0.005% to about 50%, more typically from about 0.05% to about 30% by weight of the composition.

Plasticizers for the graft copolymer are especially useful in the personal care compositions herein. Suitable plasticizers include any known or otherwise effective plasticizer suitable for use in hair care or other personal care compositions, nonlimiting examples of which include glycerin, diisobutyl adipate, butyl stearate, propylene glycol, tri-C<sub>2</sub>-C<sub>8</sub> alkyl citrates, including triethyl citrate and tri-propyl, -butyl, -pentyl, etc., analogs of triethyl citrate. Triethyl citrate is preferred.

Plasticizers are typically used at levels of from about 0.01% to about 10%, by weight of the composition, preferably from about 0.05% to about 3%, more preferably from about 0.05% to about 1%. Preferably, the weight ratio of graft polymer to the plasticizer is from about 1:1 to about 40:1, preferably from about 2:1 to about 30:1, more preferably from about 3:1 to about 25:1.

Other optional ingredients include an effective amount of a non-surface active ionic strength modifier system for reducing the viscosity of the personal care composition, especially when formulated as a hair spray composition. Preferred concentrations range from at least about 0.01%, by weight of the composition. The upper limit is dependent upon the maximum amount of the ionic strength modifiers that can be present in the particular compositions hereof such that the hair setting resin remains solubilized or dispersed. As will be understood by those skilled in the art, as the ionic strength of the composition is increased, the resin will eventually fall out of solution, or otherwise no longer remain solubilized or dispersed in the hydrophilic liquid carrier. The upper limit of the ionic strength modifier system level will vary depending upon the particular ionic strength modifiers, liquid vehicle, resin, and other ingredients present in the composition. Thus, for example, the maximum amount of the ionic strength modifiers that can be used will tend to be lower for compositions with liquid vehicles containing less water, compared to compositions

with more water. Concentrations of the optional ionic strength modifier are typically range from about 0.01% to about 4%, preferably from about 0.01% to about 2%, more preferably from about 0.01% to about 0.1%, by weight of the composition

The optional ionic strength modifier system comprises a mixture of monomeric cations and anions. The ions of the ionic strength modifier system hereof are non-surface active, i.e. they do not significantly reduce surface tension. For purposes hereof, non-surface active shall mean the ions, which at a 0.5% aqueous solution concentration, reduce surface tension by no more than 5.0 dynes/cm<sup>2</sup>. Generally, the ions of the ionic strength modifier system hereof will be characterized by having, at maximum, four or less carbon atoms per charge, preferably two or less carbon atoms, in any aliphatic chain or straight or branched chain organic heterochain.

The optional ionic strength modifier system comprises monomeric ions of the type which are products of acid-base reactions. Thus, basic and acidic ions OH<sup>-</sup> and H<sup>+</sup> do not constitute part of the ionic strength modifier system hereof, although they may be present in the composition. The ions hereof are incorporated into the composition in a form such that they can exist in the composition as free ions, i.e., in dissociated form. It is not necessary that all of the ions added exist in the composition as free ions, but must be at least partially soluble or dissociated in the composition. The ionic strength modifiers can be incorporated into the hair styling compositions, for example, by addition of soluble salts, or by addition of mixtures of acids and bases, or by a combination thereof. It is a necessary aspect of the invention that both anions and cations of the ionic strength modifier system be included in the composition.

Nonlimiting examples of suitable optional cations for use in the compositions are alkali metals, such as lithium, sodium, and potassium, and alkaline-earth metals, such as magnesium, calcium, and strontium. Preferred of the divalent cations is magnesium. Preferred monovalent metal ions are lithium, sodium, and potassium, more preferably sodium and potassium. Suitable means of addition to the compositions hereof include, for example, addition as bases, e.g., hydroxides, sodium hydroxide and potassium hydroxide, and such as salts that are soluble in the liquid carrier, e.g. salts of monomeric anions such as those described below. Other nonlimiting examples of suitable cations include organic ions, such as quaternary ammonium ions and cationic amines, such as ammonium mono-, di-, and triethanolamines, triethylamine, morpholine, aminomethylpropanol (AMP), aminoethylpropanediol, etc. Ammonium and the amines are preferably provided in the forms of salts, such as hydrochloride salts.

Monomeric anions that can be used include halogen ions, such as chloride, fluoride, bromide, and iodide, particularly chloride, sulfate, ethyl sulfate, methyl sulfate, cyclohexyl sulfamate, thiosulfate, toluene sulfonate, xylene sulfonate, citrate, nitrate, bicarbonate, adipate, succinate, saccharinate, benzoate, lactate, borate, isethionate, tartrate, and other monomeric anions that can exist in dissociated form in the hair styling composition. The anions can be added to the compositions hereof, for example, in the form of acids or salts which are at least partially soluble in the liquid vehicle, e.g., sodium or potassium salts of acetate, citrate, nitrate, chloride, sulfate, etc. Preferably, such salts are entirely soluble in the vehicle.

The use of optional ionic strength modifiers are especially useful in reduced volatile organic solvent compositions.

Other optional ingredients include surfactants (which may be anionic, cationic, amphoteric, or zwitterionic and which include fluorinated surfactants and silicone copolyols), propellants, hair conditioning agents (e.g., silicone fluids, fatty esters, fatty alcohols, long chain hydrocarbons, cationic surfactants, etc.); emollients; lubricants and penetrants such as various lanolin compounds; protein hydrolysates and other protein derivatives; ethylene adducts and polyoxyethylene cholesterol; dyes, tints, bleaches, reducing agents and other colorants; pH adjusting agents; sunscreens; preservatives; thickening agents (e.g. polymeric thickeners, such as xanthan gum); and perfume.

#### Method of Use

The personal care compositions of the present invention are used in conventional ways to provide the desired personal care benefit. For hair spray or other hair styling compositions, the composition is used in a conventional way to provide the desired hair styling/holding benefits of the present invention, which typically involves application of an effective amount of the composition to dry, slightly damp, or wet hair before and/or after the hair is arranged to a desired style. The composition is then dried or allowed to dry onto the applied surface.

The term "effective amount" as used in this context means an amount of the personal care composition or hair styling composition sufficient to provide the desired benefit. In the case of hair spray and other hair styling compositions, an effective amount of the composition is applied to the hair to provide the hold and style benefits desired considering the length and texture of the hair. In general, from about 0.5g to about 30g of such hair spray or other hair styling composition will be applied to the hair, depending upon the particular product formulation, dispenser type, length of hair, type of hair style, and so forth.

### EXAMPLES

The following non-limiting examples illustrate specific embodiments of the process limitations of the present invention, graft polymers made in accordance with such process limitations, and hair styling and other personal care compositions comprising these graft polymers. It is understood, however, that various additions or modifications of the specific exemplified embodiments can be made without departing from the spirit and scope of the invention. It is intended to cover, in the appended claims, all such modifications that are within the scope of the subject invention.

#### Example 1

The hydrophilic graft polymers 1.1 and 1.2 described in the following example are prepared in accordance with the process limitations of the present invention. Specific embodiments of such process limitations are described for each of the hydrophilic graft polymers.

##### Graft Polymer 1.1

Poly(2-methoxyethyl acrylate-co-methacrylic acid-co-tert-butyl acrylate-co-4-chloromethyl styrene)-graft-poly(styrene-co-methacrylic acid)

Into an argon purged round-bottomed-flask equipped with mechanical stirring and a reflux condenser, is added butyl acetate (1L), trimethylsilylmethacrylate (18.4g, 0.116 mole), tert-butylacrylate (27.2g, 0.212 mole), 2-methoxyethyl acrylate (31.4g, 0.241mole), and chloromethyl styrene (0.4g, 0.003 mole). The solution is heated to 60°C then initiated with AIBN (azobisisobutyronitrile) (0g, 0.006 mole) and allowed to undergo free radical polymerization for 10 hours. The resulting solution is then heated to 100°C and allowed to cool. When the solution reaches ambient temperature, trimethylsilylmethacrylate (22.0g, 0.139 mole), styrene (18.0g, 0.173mole), 2,2'-dipyridyl (1.4g, 0.009 mole), and Cu(I)Cl (0.3g, 0.003 mole) are added. The solution is then heated to 120°C with stirring for 6 hours. The solution is then cooled to ambient temperature and catalyst is removed via vacuum filtration. The filtrate is diluted with acetone (200 ml) and water (10 ml) and stirred for 2 hours. The resulting solution is precipitated into hexanes and the graft polymer collected and dried.

Graft Polymer 1.2

Poly(2-methoxyethyl acrylate-co-methacrylic acid-co-tert-butyl acrylate-co-4-chloromethyl styrene)-graft-[poly(styrene-co-methacrylic acid); poly(dimethylsiloxane)]

Into an argon purged round-bottomed-flask equipped with mechanical stirring and a reflux condenser, is added butyl acetate (1L), trimethylsilyl methacrylate (18.4g, 0.116 mole), tert-butylacrylate (27.2g, 0.212 mole), 2-methoxyethyl acrylate (26.4g, 0.203 mole), polydimethylsiloxane macromonomer (molecular weight 10,000)(available from Chisso Corp., Tokyo, Japan) (5g), and chloromethyl styrene (0.4g, 0.003 mole). The solution is heated to 60°C then initiated with AIBN (1.0g, 0.006 mole) and allowed to undergo free radical polymerization for 10 hours. The resulting solution is then heated to 100°C then allowed to cool. When solution reaches ambient temperature, trimethylsilylmethacrylate (22.0g, 0.139 mole), styrene (18.0g, 0.173mole), 2,2'-dipyridyl (1.4g, 0.009 mole), and Cu(I)Cl (0.3g, 0.003 mole) are added. The solution is heated to 120°C with stirring for 6h. The solution is then cooled to ambient temperature and catalyst is removed via vacuum filtration. Filtrate is diluted with acetone (200 ml) and water (10 ml) and stirred for 2 hours. The resulting solution is precipitated into hexanes and the graft polymer collected and dried.

Example 2

The hydrophobic graft polymer 2.0 described in the following example is prepared in accordance with the process limitations of the present invention. Specific embodiments of such process limitations are described for each of the hydrophobic graft polymers.

Graft Polymer 2.0

Poly(tert-butyl acrylate-co-2-ethylhexyl methacrylate-co-chloromethyl styrene)-graft-poly(n-butyl acrylate)

Into an argon purged round-bottomed-flask equipped with mechanical stirring and a reflux condenser, is added butyl acetate (1L), tert-butyl acrylate (54 g, 0.417 mole), 2-ethylhexyl methacrylate (10g, 0.050 mole), and chloromethyl styrene (6g, 0.039 mole). The solution is heated to 60 °C and then initiated with AIBN (0.6g,

0.004 mole) and allowed to undergo free radical polymerization for 12 hours. The resulting solution is heated to 100°C then allowed to cool. When solution reaches ambient temperature, n-butyl acrylate (30g, 0.211 mole), 2,2'-dipyridyl (18.3g, 0.117 mole), and Cu(I)Cl (3.9g, 0.039 mole) are added. The solution is heated to 120°C with stirring for 6 hours. The solution is then cooled to ambient temperature and catalyst is removed via vacuum filtration. The filtrate is diluted with acetone (200 ml) and water (10 ml) and stirred for 2 hours. The resulting solution is precipitated into hexanes and the graft polymer collected and dried.

### Examples 3-10

The following Examples 3-10 represent nonaerosol hair spray embodiments of the compositions of the present invention.

Component (wt%)	<u>Example No.</u>							
	3	4	5	6	7	8	9	10
Graft copolymer 1.1	4.00	5.00	6.00	4.00	---	---	---	---
Graft copolymer 1.2	---	---	---	---	3.00	3.50	2.50	4.00
Isododecane <sup>1</sup>	1.00	---	---	---	---	1.0	2.0	---
Diisobutyl adipate	0.40	---	0.90	0.55	---	---	---	0.40
Sodium hydroxide <sup>2</sup>	0.96	1.20	1.44	---	---	1.20	---	1.35
Potassium hydroxide <sup>3</sup>	--	--	--	1.21	1.00	--	0.70	--
Perfume	0.10	0.10	0.10	0.10	0.10	0.15	0.10	0.15
Sodium Benzoate	--	--	--	--	0.10	0.10	--	0.10
Ethanol <sup>4</sup>	76.54	71.95	81.56	71.25	79.40	69.26	78.00	55.00
Water	QS10	QS10	QS10	QS10	QS10	QS10	QS10	QS10
	0	0	0	0	0	0	0	0

<sup>1</sup> PERMETHYL 99A, from Presperse, Inc., South Plainfield, NJ, USA.

<sup>2</sup> Sodium hydroxide is 30% active.

<sup>3</sup> Potassium hydroxide is 45% active.

<sup>4</sup> SDA 40 (100% ethanol).

Examples 11-16

The following Examples 11-16 represent aerosol hair spray embodiments of the compositions of the present invention.

Component (wt%)	<u>Example No.</u>					
	11	12	13	14	15	16
Graft copolymer 1.1	5.00	4.00	3.50	---	---	---
Graft copolymer 1.2	---	---	---	4.00	3.00	4.00
Isododecane <sup>1</sup>	0.50	---	---	--	--	0.50
Triethyl citrate <sup>2</sup>	--	--	0.21	--	--	--
Diisobutyl adipate	0.70	0.45	--	0.40	0.25	0.35
Propylene glycol	--	--	0.30	--	---	---
Sodium hydroxide <sup>3</sup>	1.00	--	--	--	1.0	---
Potassium hydroxide <sup>4</sup>	--	0.94	1.20	1.04	---	1.20
Perfume	0.10	0.10	0.10	0.10	0.10	0.10
Sodium Benzoate	0.10	0.10	--	0.10	0.20	--
Ethanol <sup>5</sup>	56.69	57.42	72.0	50.0	30.00	54.5
Propellant - isobutane	--	--	7.02	15.00	10.00	--
Propellant - n-butane	10.00	---	--	--	--	--
Propellant - dimethyl ether <sup>6</sup>	10.00	---	--	15.00	15.00	--
Propellant - Hydrofluorocarbon 152a <sup>7</sup>	--	25.0	15.98	--	--	32.32
Water	QS100	QS100	QS100	QS100	QS100	QS100

<sup>1</sup> PERMETHYL 99A, from Presperse, Inc., South Plainfield, NJ, USA.

<sup>2</sup> CITROFLEX-2, from Morflex, Inc., Greensboro, NC, USA.

<sup>3</sup> Sodium hydroxide is 30% active.

<sup>4</sup> Potassium hydroxide is 45% active.

<sup>5</sup> SDA 40 (100% ethanol).

<sup>6</sup> DYMEL - A, from Dupont.

<sup>7</sup> DYMEL-152a, from Dupont.

Each of the exemplified personal care compositions (Examples 3-16) are hair spray or hair styling embodiments of the compositions of the present invention, and comprise graft polymer as a styling or film-forming polymer made in accordance with the synthetic methods of the present invention. Each of the compositions may be formulated by conventional or otherwise known formulation and mixing techniques. For example, each of the graft polymers is first mixed with the ethanol, neutralizing



the polymer with sodium or potassium hydroxide, then adding sequentially (as applicable) with mixing, isododecane, plasticizer, perfume, and water. If sodium benzoate is used, it is added after water addition. Most preferably a premix of water and sodium benzoate is made and then added after the main water addition. Propellants for aerosol compositions are charged to conventional aerosol containers after the remainder of the prepared composition has been added.

#### EXAMPLE 17

The following represents a hair styling gel embodiment of the composition of the present invention.

<u>Ingredients</u>	<u>Weight %</u>
Graft copolymer 1.2	2.50
Water	QS 100%
Carbomer 940	0.50
Sodium Hydroxide Solution (30% by weight)	0.80
Panthenol	0.05
Polysorbate 80	0.20
Perfume	0.20

This product is prepared by dispersing graft copolymer and carbomer 940 in water and adding sodium hydroxide. The mixture is stirred for about 0.5 hour before adding the remaining ingredients.

#### EXAMPLE 18

The following represents a spray-on gel embodiment of the composition of the present invention.

<u>Ingredients</u>	<u>Weight %</u>
Water	Q.S. to 100 %
Ethanol	15.00
Panthenol	0.05
Potassium Hydroxide Solution (45% by weight)	0.50
Perfume	0.20
Graft copolymer 1.1	2.00

This composition is prepared by dissolving the graft copolymer 1.1 in ethanol and then adding water and potassium hydroxide solution to facilitate the

incorporation of the copolymer into the solvent. The mixture is stirred for about 0.5 hour before adding the remaining ingredients.

### EXAMPLE 19

The following represents a hair styling mousse embodiment of the composition of the present invention.

<u>Ingredients</u>	<u>Weight %</u>
Water	Q.S. to 100 %
Lauramine Oxide	0.20
Panthenol	0.05
Perfume	0.05
Copolymer 1.2	3.00
Sodium Hydroxide Solution (30% by weight)	1.00
Isobutane	7.00

This composition is prepared by dissolving the graft copolymer 1.2 in water and then adding sodium hydroxide solution with mixing for about 0.5 hour. The other ingredients, except isobutane, are added and mixed for an additional 10 minutes. Aluminum aerosol cans are then filled with 93 parts of this batch, affixed with a valve which is crimped into position, and lastly pressure filled with 7 parts Isobutane. This composition is useful for application to the hair to provide conditioning, styling and hold.

### EXAMPLE 20

The following example represents a topical sun screen embodiment of the composition of the present invention.

<u>Ingredients</u>	<u>Weight %</u>
Water	QS100
Carbomer 1342 <sup>[1]</sup>	0.16
Octyl Methoxycinnamate	0.50
Dimethicone copolyol	0.10
Tocopheryl Acetate	0.10
Sodium Hydroxide (30% sol. by weight)	1.50
Ethanol	40.00
Copolymer 1.2	4.00

[1] Available as Carbopol® 1342 from B.F. Goodrich.

The water, ethanol, sodium hydroxide solution and polymer 4 are mixed for one half hour. The remaining ingredients are added and mixed for an additional half hour.

This composition is prepared by combining and mixing the graft copolymer 1.2 and water, ethanol, sodium hydroxide solution. The remaining ingredients are then added to the mixture.

#### EXAMPLE 21

The following example represents a topical skin care embodiment of the composition of the present invention.

<u>Ingredients</u>	<u>Weight %</u>
Graft copolymer 1.2	2.00
Water	Q.S. to 100 %
Ethanol (SDA 40)	40.00
Carbomer 940	0.75
Sodium Hydroxide Solution (30% by weight)	0.90
Salicylic Acid	2.00

The composition is prepared by mixing water, ethanol, graft copolymer, and carbomer together for about 10 minutes. The remaining ingredients are added and the mixture is stirred for an additional 30 minutes. This composition is useful for application to the skin to provide improved water resistance and is useful in treating acne.

#### EXAMPLE 22

The following example represents a nail polish embodiment of the composition of the present invention. The composition is prepared by combining and mixing all of the listed ingredients until uniformly dispersed throughout the composition.

<u>Ingredients</u>	<u>Weight %</u>
Graft copolymer 1.1	15.00
Ethanol	42.00
Acetone	40.00
NaOH soln., 30%	3.00

EXAMPLE 23

The following example represents a topical skin care embodiment of the composition of the present invention. The topical composition is intended for use in treating, preventing or otherwise reducing the appearance of wrinkles on human skin. The composition is prepared by combining and mixing all of the listed ingredients until uniformly dispersed throughout the composition.

<u>Ingredients</u>	<u>Weight %</u>
Graft copolymer 1.1	6.00
NaOH soln., 30%	2.10
DRO Water (purified by double reverse osmosis)	q.s.

EXAMPLE 24

The following example represents a hair styling lotion embodiment of the composition of the present invention. The graft copolymer is dissolved in ethanol and then added and mixed with the remaining ingredients until uniformly dispersed throughout the composition.

<u>Ingredients</u>	<u>Weight %</u>
Graft copolymer 1.1	4.00
Natrosol 250HH <sup>1</sup>	0.50
NaOH soln., 30%	1.35
Kathon CG	0.03
Ethanol	8.00
DRO water	q.s.

<sup>1</sup> Natrosol 250HH-Hydroxyethylcellulose offered by Aqualon.

EXAMPLE 25

The following example represents an aftershave embodiment of the composition of the present invention. The composition is prepared by combining and mixing all of the listed ingredients until uniformly dispersed throughout the composition.

<u>Ingredients</u>	<u>Weight %</u>
Graft copolymer 1.2	2.00
NaOH soln., 30%	0.60
Ethanol	50.00

Perfume	0.20
Menthol	0.20
DRO water	q.s.

Examples 26-28

The following examples represent hair styling/conditioning rinse embodiments of the compositions of the present invention.

<u>Composition</u>	<u>Example No.</u>		
	<u>26</u>	<u>27</u>	<u>28</u>
<u>Conditioner Premix</u>			
Water	q.s.	q.s.	q.s.
Citric Acid	0.02	0.02	0.02
Sodium Citrate	0.09	0.09	0.10
Cetyl Alcohol	0.12	0.12	0.12
Stearyl Alcohol	0.08	0.08	0.08
Natrosol Plus CS Grade D-67 <sup>1</sup>	1.02	1.00	0.99
Xanthan Gum <sup>2</sup>	0.25	0.25	0.25
<u>Styling Polymer Premix</u>			
Graft polymer 2.0	1.75	1.75	1.75
Permethyl 99A	8.54	8.54	8.54
Trimethylsiloxysilicate	0.11	0.11	0.11
Kathon CG	0.03	0.03	0.03
Perfume	0.33	0.33	0.33
<u>Silicone Premix</u>			
DRO Water	9.48	9.48	8.57
Adogen 470 <sup>4</sup>	0.70	0.60	0.93
Adogen 471 <sup>5</sup>	0.05	0.15	0.07
Decamethyl cyclopentasiloxane/ Polydimethyl Siloxane Gum <sup>3</sup>	1.67	1.67	2.33
Triethylsilyl Amodimethicone (Dow Corning Q2-8220)	0.10	0.10	0.10
<u>Surfactant Premix</u>			
DRO Water	5.70	5.70	5.70
Stearalkonium Chloride	0.30	0.30	0.30

<sup>1</sup>Hydrophobically modified hydroxyethyl cellulose from Aqualon Corp.

<sup>2</sup>Readily dispersible xantham gum

<sup>3</sup>SE-76 gum available From General Electric

<sup>4</sup>Ditallow dimethyl ammonium chloride, Sherex Chemical Co., Dublin, Ohio, USA; 75% aqueous solution

<sup>5</sup>Tallow trimethyl ammonium chloride, Sherex Chemical Co.; 50% aqueous solution.

Each of the exemplified compositions are prepared as follows. A silicone premix is prepared by combining and mixing (in a separate vessel ) water, Adogen 470 and Adogen 471 at 85°C. Cool to 71°C and add the silicone gum/decamethyl cyclopentasiloxane solution and amodimethicone and mix until homogeneous. Cool to 38°C while using a homogenizer (such as Tekmar). Prepare the surfactant premix by combining and mixing (in a second and separate vessel) water and Stearalkonium Chloride at 38°C. Prepare the conditioner premix by combining and mixing (in a third and separate vessel) DRO water heated to 71°C, citric acid, sodium citrate, cetyl alcohol, stearyl alcohol and Natrosol Plus CS grade D-67, and until uniformly dispersed, and then add xanthan gum and mix until uniformly dispersed. Prepare the styling polymer premix by combining and mixing the graft polymer, permethyl 99A, and Trimethylsiloxysilicate until a uniform mixture is obtained.

Combine and mix the styling polymer premix, Kathon CG and perfume until homogeneous. Further dispersed with an in-line homogenizer (such as Tekmar homogenizer) and then cool the mixture to 38°C. Complete the conditioner by adding the conditioner premix, the silicone premix and the surfactant premix at 38°C. Mix until homogeneous, then cool the composition to 25 °C.

When the compositions defined in Examples 26-28 are applied to hair in the conventional manner, they provide effective hair conditioning and styling/hold benefits without leaving the hair with a sticky/stiff feel.

#### EXAMPLE 29

##### Polymer Premix with added Drying Aid

<u>Ingredients</u>	<u>Weight %</u>
Graft copolymer 2.0	16.83
Permethyl 99A	82.17
Trimethylsiloxysilicate	1.00

This polymer premix is prepared by adding the graft copolymer to the solvents while mixing. The mixture is heated to between 80°C and 84°C in a covered vessel while mixing, and then cooled to between 23°C and 27°C before adding trimethylsiloxysilicate while mixing.

EXAMPLE 30Polymer Premix with added Drying Aid

<u>Ingredients</u>	<u>Weight %</u>
Graft copolymer 2.0	15.00
Isododecane	83.50
Polydimethylsiloxane <sup>2</sup>	1.50
<sup>2</sup> Polydimethylsiloxane, Dow Corning, Dow Corning 200 Fluid (20 csk)	

This polymer premix is prepared by adding the graft copolymer to the solvents while mixing. The mixture is heated to between 80°C and 84°C in a covered vessel while mixing, and then cooled to between 23°C and 27°C before adding trimethylsiloxysilicate while mixing.

EXAMPLE 31

The following example represents a hair conditioning embodiment of the composition of the present invention.

<u>Ingredient</u>	<u>Weight %</u>	
	<u>A</u>	<u>B</u>
<u>Styling Agent Premix</u>		
Graft copolymer Premix of Example 30	10.00	10.00
<u>Silicone Premix</u>		
Silicone gum, GE SE76 <sup>2</sup>	0.30	0.30
Octamethyl cyclotetrasiloxane	1.70	1.70
<u>Main Mix</u>		
Water	QS100	QS100
Cetyl Alcohol	1.00	----
Quaternium 18 <sup>3</sup>	0.85	0.85
Stearyl Alcohol	0.70	----
Hydroxethyl Cellulose	0.50	----
Cetyl Hydroxyethyl Cellulose <sup>4</sup>	----	----
1.25		
Cetareth-20	0.35	----
Fragrance	0.20	0.20

Dimethicone copolyol	0.20	----
Citric Acid	0.13	0.13
Methylchloroisothiazolinone (and) methylisothiazolinone	0.04	0.04
Sodium Chloride	0.01	0.01
Xanthan Gum	----	
0.20		

Each of the compositions is prepared by comixing all the Main Mix ingredients, heating the resulting mixture to about 60°C with mixing. The heated mixture is then cooled to about 45°C with colloid milling (Example A) or mixing (Example B). At this temperature, the two premixes are added separately with moderate agitation and the resulting conditioner is allowed to cool to room temperature. This composition is useful as a rinse off hair conditioner.

<sup>2</sup> Commercially available from General Electric.

<sup>3</sup> Dimethyl Di(Hydrogenated Tallow) Ammonium Chloride

<sup>4</sup> Commercially available as Polysurf D-67 from Aqualon.

### EXAMPLE 32

The following example represent a shampoo embodiment of the composition of the present invention.

<u>Ingredients</u>	<u>Weight %</u>
<u>Styling Agent</u>	
Copolymer Premix from Example 30	15.00
<u>Premix</u>	
Silicone gum	0.50
Dimethicone, 350 cs fluid	0.50
<u>Main Mix</u>	
Water	QS100
Ammonium lauryl sulfate	11.00
Cocamide MEA	2.00
Ethylene glycol distearate	1.00
Xanthan Gum	1.20
Methylchloroisothiazolinone (and)	



methylothiazolinone	0.04
Citric Acid to pH 4.5 as needed	

The Main Mix is prepared by first dissolving xanthan gum in water with conventional mixing. The remaining Main Mix ingredients are added and the Main Mix is heated to 150°F with agitation for about 0.5 hour. The Styling Agent and the Premix are then added sequentially with about 10 minutes of agitation between additions, and the entire mixture is stirred while the batch is cooled to room temperature. For varied particle size, the Styling Agent and Premix can be added at different times using either or both high shear mixing (high speed dispersator) or normal agitation. This shampoo composition is useful for cleansing the hair and for providing a styling benefit.

What is claimed is:

1. Personal care compositions comprising

(a) from 0.1% to 15% by weight of a graft polymer made in accordance with the following process steps:

(i) reacting copolymerizable monomers to form an organic polymeric backbone having a weight average molecular weight of from 15,000 grams/mole to 9,800,000 grams/mole and a plurality of organic halide moieties covalantly bonded to and pendant from the polymeric backbone; and then

(ii) reacting copolymerizable monomers with the organic halide moieties of the polymeric backbone by atom transfer free radical polymerization in the presence of a catalytic amount of a Cu(I) salt to form a plurality of polymeric side chains covalently bonded to and pendant from the polymeric backbone, the polymeric side chains having an average molecular weight of from 500 grams/mole to 200,000 grams/mole; wherein the polymeric backbone and the plurality of polymeric side chains form graft polymers having a weight average molecular weight of from 16,000 grams/mole to 10,000,000 grams/mole; and

(b) from 0.1% to 99.9% by weight of a liquid carrier.

2. The composition of Claim 1 wherein the graft polymer is hydrophilic and the liquid carrier is selected from the group consisting of water, ethanol, *n*-propanol, isopropanol, and combinations thereof.

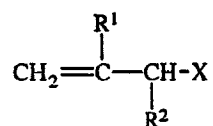
3. The composition of any one of the preceding Claims wherein the Cu(I) salts are selected from the group consisting of Cu(I)Br, Cu(I)Cl, Cu(I)I, Cu(I) thiocyanate, and combinations thereof, and wherein the reaction of step (a) is free radical polymerization of the copolymerizable monomers.

4. The composition of any one of the preceding Claims wherein the Cu(I) salt is in the form of a ligand complex, wherein the ligand is an aprotic bidentate selected from the group consisting of 2,2' dipyridyl, diphosphates, 4,4'-di-5-nonyl-2,2'-bipyridine, 4,4'-di-tert-butylbipyridine, 4,4'-diheptyl-2,2'-bipyridine, and combinations thereof.

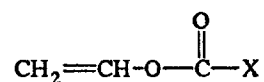
5. The composition of any one of the preceding claims wherein the copolymerizable monomers of step (a) comprise an organic halide-containing vinyl monomer and a second monomer selected from the group consisting of acrylic acid produced by hydrolysis of trimethylsilyl acrylate, methacrylic acid produced by hydrolysis of trimethylsilyl methacrylate, vinyl pyrrolidone, acrylic acid esters of C<sub>1</sub>-C<sub>18</sub> alcohols, methacrylic acid esters of C<sub>1</sub>-C<sub>18</sub> alcohols, trimethylsilyl acrylate, trimethylsilyl methacrylate, styrene, alpha-methylstyrene, t-butylstyrene, vinyl acetate, vinyl propionate, 2-methoxyethyl acrylate, 2-ethoxyethyl acrylate, n-butyl methacrylate, isobutyl methacrylate, t-butyl acrylate, t-butyl methacrylate, 2-ethylhexyl methacrylate, methyl methacrylate, salts thereof, and mixtures thereof.

6. The composition of Claim 5 wherein the organic halide-containing vinyl monomer of step (a) is selected from the group consisting of

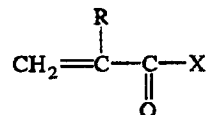
(I)



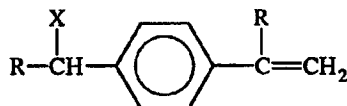
(II)



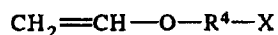
(III)



(IV)



(V)



and combinations thereof, wherein R is methyl or hydrogen; X is a halogen atom; R<sup>1</sup> and R<sup>2</sup> are each independently methyl, hydrogen or methoxy; and R<sup>4</sup> is an alkyl group having from 1 to 8 carbon atoms.

7. The composition of any one of the preceding claims wherein the polymeric backbone represents from 50% to 99% by weight of the graft polymer, and the plurality of polymeric side chains represent from 1% to 50% by weight of the graft polymer.

8. The composition of any one of Claims 1, 2, 3 or 4 wherein the graft polymer has a polymeric backbone having a T<sub>g</sub> value of less than 10°C and a plurality of polymeric side chains having a T<sub>g</sub> value greater than 70°C.

9. The composition of any one of Claims 1, 2, 3 or 4 wherein the graft polymer has a polymeric backbone having a T<sub>g</sub> value greater than 50°C and a plurality of polymeric side chains having a T<sub>g</sub> value less than -20°C.

10. The composition of any one of Claims 1, 2, 3 or 4 wherein the graft polymer is hydrophobic and the liquid carrier comprises a hydrophobic liquid carrier selected from the group consisting of volatile branched chain hydrocarbons having from 12 to 16 carbon atoms, liquid silicone carriers, and combinations thereof, wherein the liquid silicone carriers are selected from the group consisting of phenyl pentamethyl disiloxane, phenylethyl pentamethyl disiloxane, hexamethyl disiloxane, methoxypropyl heptamethyl cyclotetrasiloxane, chloropropyl pentamethyl disiloxane, hydroxypropyl pentamethyl disiloxane, cyclomethicones, including octamethyl cyclotetrasiloxane, decamethyl cyclopentasiloxane, and mixtures thereof.

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/IB 98/00753

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 A61K7/00 C08F291/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 A61K C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 96 30421 A (MATYJASZEWSKI KRZYSZTOF ;WANG JIN SHAN (US)) 3 October 1996 see page 39, line 16 - page 40, line 4; claim 1	1-10
Y	WO 95 01383 A (PROCTER & GAMBLE) 12 January 1995 see page 3, line 10-25; claims 1,7-10	1-10



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

\* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

8 September 1998

Date of mailing of the international search report

22/09/1998

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Meulemans, R

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/IB 98/00753

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9630421 A	03-10-1996	US 5763548 A	09-06-1998
		AU 5306996 A	16-10-1996
		CA 2216853 A	03-10-1996
		CN 1183107 A	27-05-1998
		EP 0817806 A	14-01-1998
WO 9501383 A	12-01-1995	AU 7253294 A	24-01-1995
		AU 7320094 A	24-01-1995
		BR 9407017 A	10-09-1996
		BR 9407018 A	10-09-1996
		CA 2165767 A	12-01-1995
		CA 2165768 A	12-01-1995
		CN 1129946 A	28-08-1996
		CN 1129945 A	28-08-1996
		CZ 9503492 A	12-06-1996
		CZ 9503493 A	12-06-1996
		EP 0706536 A	17-04-1996
		EP 0706537 A	17-04-1996
		HU 74037 A	28-10-1996
		HU 74034 A	28-10-1996
		JP 8512083 T	17-12-1996
		JP 8512084 T	17-12-1996
		WO 9501384 A	12-01-1995
		US 5730966 A	24-03-1998





**PCT**WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup> :</b> <b>C09J 151/00, A61K 7/48</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 98/51755</b> <b>(43) International Publication Date:</b> 19 November 1998 (19.11.98)
<b>(21) International Application Number:</b> PCT/IB98/00702 <b>(22) International Filing Date:</b> 11 May 1998 (11.05.98)  <b>(30) Priority Data:</b> 08/854,698                      12 May 1997 (12.05.97)                      US  <b>(71) Applicant:</b> THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US).  <b>(72) Inventors:</b> MIDHA, Sanjeev; Apartment 2D, 9274 Deercross Parkway, Blue Ash, OH 45236 (US). NIJAKOWSKI, Timothy, Roy; Apartment 15, 4003 Sharon Park Lane, Cincinnati, OH 45241 (US).  <b>(74) Agents:</b> REED, T. David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217 (US).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> TOUGHENED GRAFTED POLYMERS  <b>(57) Abstract</b>  An adhesive copolymer and personal care composition thereof, said copolymer being characterized by an organic polymeric backbone wherein said backbone has a Tg of from 0 °C to 45 °C wherein said copolymer comprises one or more side chains grafted thereon consisting of acrylic and methacrylic monomer units wherein (each of) said side chains have a Tg of greater than 50 °C–200 °C wherein the number average molecular weight of said side chain is greater than 1000.		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

## TOUGHENED GRAFTED POLYMERS

## TECHNICAL FIELD

The present invention relates to toughened grafted polymers.

## BACKGROUND OF THE INVENTION

5       Cosmetic compositions such as lotions, creams, emulsions, packs, make-up (e.g., foundations, lipsticks, eye shadows and the like) and hair compositions are used to improve one's outward appearance. Many personal care products contain various resins, gums, and adhesive polymers. The polymers are used for a variety of purposes including thickening, feel properties, film-forming ability, active deposition, active penetration, hair holding, etc.

10       Consequently there is constantly a search for developing polymers having improved properties for use in personal care product. For example, the desire to have the hair retain a particular shape is widely held. The most common methodology for accomplishing this is the application of a styling composition to dampened hair, after shampooing and/or conditioning, or to dry, styled hair. These compositions provide temporary setting benefits

15       and they can be removed by water or by shampooing. The materials used in the compositions to provide the setting benefits have generally been resins and have been applied in the form of mousses, gels, lotions or sprays.

      Many people desire a high level of style retention, or hold, from a hair spray composition. In typical hair sprays, hold is achieved by the use of resins, such as

20       AMPHOMER®, supplied by National Starch and Chemical Company, and GANTREZ® SP 225, supplied by GAF. In general, as hair hold for hair spray compositions is increased, the tactile feel of the hair becomes stiffer and hence, less desirable. It is desirable to provide hair spray products which could provide an improved combination of hair hold and hair feel characteristics.

25       Recently, it has become known to utilize silicone grafted organic backbone polymers in various personal care compositions including their use as hair setting agents in hairspray compositions and other hair styling compositions, e.g. hair tonics, lotions, rinses, mousses, etc. Silicone grafted polymers can be used to make personal care compositions with improved feel, e.g., in the case of hair sprays, increased softness relative to

30       conventional polymeric hair setting agents.

      It remains desirable to improve the performance of grafted polymers. It is an object of this invention to provide toughened graft copolymers which can be used in, for example, personal care compositions.

      It is a further object of this invention to provide toughened graft copolymers that

35       have improved adhesive and cohesive properties and low creep at high humidity thereby providing improved style durability benefits.

These and other benefits as may be apparent from the description below can be obtained by the present invention.

The present compositions can comprise, consist of, or consist essentially of any of the required or optional ingredients and/or limitations described herein.

5 All percentages and ratios are calculated on a weight basis unless otherwise indicated. All percentages are calculated based upon the total composition unless otherwise indicated.

All ingredient levels refer to the active level of that ingredient, and are exclusive of solvents, by-products, or other impurities that may be present in commercially available  
10 sources, unless otherwise indicated.

#### SUMMARY OF THE INVENTION

The present invention relates to an adhesive copolymer, said copolymer being characterized by an organic polymeric backbone wherein said backbone has a Tg of from about 0°C to about 45°C wherein said copolymer comprises one or more side chains grafted  
15 thereon consisting of acrylic and methacrylic monomer units wherein each of said side chains has a Tg of greater than about 50°C - 200°C wherein the number average molecular weight of said side chain is greater than about 1000.

By adhesive polymer what is meant is that when applied as a solution to a surface and dried, the polymer forms a film or a weld. Such a film will have adhesive and cohesive  
20 strength, as is understood by those skilled in the art.

#### DETAILED DESCRIPTION OF THE INVENTION

The essential components of the present invention are described below. Also included is a nonexclusive description of various optional and preferred components useful in embodiments of the present invention.

##### 25 Grafted Adhesive Polymer

The grafted polymers are characterized by acrylic and methacrylic monomer units covalently bonded to and pendant from a polymeric carbon-based backbone.

The backbone will preferably be a carbon chain derived from polymerization of ethylenically unsaturated monomers and wherein said backbone has a Tg of from about 0°C  
30 to about 45° C.

The grafted polymer should have a weight average molecular weight of at least about 20,000. There is no upper limit for molecular weight except that which limits applicability of the invention for practical reasons, such as processing, aesthetic characteristics, formulateability, etc. In general, the weight average molecular weight will be  
35 less than about 10,000,000, more generally less than about 5,000,000, and typically less than about 3,000,000. Preferably, the weight average molecular weight will be between

about 50,000 and about 2,000,000, more preferably between about 75,000 and about 1,000,000, most preferably between about 80,000 and about 750,000.

The term "graft copolymers" is familiar to one of ordinary skill in polymer science and is used herein to describe the copolymers which result by adding or "grafting" polymeric side chain moieties (i.e. "grafts") onto another polymeric moiety referred to as the "backbone".  
5 The backbone typically has a higher molecular weight than the grafts. Thus, graft copolymers can be described as polymers having pendant polymeric side chains, and as being formed from the "grafting" or incorporation of polymeric side chains onto or into a polymer backbone. The polymer backbone can be a homopolymer or a copolymer. The  
10 graft copolymers are derived from a variety of monomer units.

The graft polymers made in accordance with the methods herein can have a single Tg and preferably are copolymers having at least two distinct immiscible phases, wherein the polymeric side chains are closely associated with each other and exist in one phase and polymeric backbone of the copolymer remains in a second separate phase. A consequence  
15 of this phase immiscibility is that if the temperature separation between each of the Tg's values involved is large enough then these copolymers exhibit two distinct Tg's, namely one Tg value for the backbone and one Tg value for the side chain. The term Tg means glass transition temperature, which is familiar to one of ordinary skill in the art. The copolymers can also exhibit a third glass transition temperature corresponding to any optional  
20 polysiloxane side chains on the graft copolymers. Whether such a third Tg value is observable depends upon a number of factors including the percent silicone in the copolymer, the number of polysiloxane side chains in the copolymer, the temperature separation between each of the Tg's values involved, and other such physical factors.

#### Backbone Vinyl Monomer Units:

25 The copolymers of the present invention comprise from about 50% to about 98%, preferably from about 60% to about 95%, and more preferably from about 70% to about 90% by weight of the backbone vinyl monomer units.

The backbone vinyl monomer unit is selected from copolymerizable monomers, preferably ethylenically unsaturated monomers. The monomers are selected to meet the  
30 requirements of the copolymer. By "copolymerizable", as used herein, is meant that the vinyl monomer can be reacted with or polymerized with the acrylic or methacrylic macromonomers in a polymerization reaction using one or more conventional synthetic techniques, such as ionic, emulsion, dispersion, Ziegler-Natta, free radical, group transfer or step growth polymerization. In the present invention, monomers and macromonomers that  
35 are copolymerizable using conventional free radical initiated techniques are preferred. The term "ethylenically unsaturated" is used herein to mean a material that contains at least one polymerizable carbon-carbon double bond, which can be mono-, di-, tri- or tetra-substituted.

The monomer units can be derived from hydrophilic monomers (typically polar monomers), or mixtures of such hydrophilic monomers with hydrophobic monomers (typically low polarity monomers), provided that the solubility characteristics of the overall copolymer is achieved. As used herein, "hydrophilic monomers" means monomers which  
5 form homopolymers which are substantially water soluble; "hydrophobic monomers" means monomers which form substantially water insoluble homopolymers.

Preferred monomers include unsaturated alcohols, unsaturated monocarboxylic acids, unsaturated dicarboxylic acids, unsaturated anhydrides, alcohol esters of unsaturated monocarboxylic acids, alcohol esters of unsaturated dicarboxylic acids, alcohol esters of  
10 unsaturated anhydrides, alkoxylated esters of unsaturated monocarboxylic acids, alkoxylated esters of unsaturated dicarboxylic acids, alkoxylated esters of unsaturated anhydrides, aminoalkyl esters of unsaturated monocarboxylic acids, aminoalkyl esters of unsaturated dicarboxylic acids, aminoalkyl esters of unsaturated anhydrides, amides of unsaturated monocarboxylic acids, amides of unsaturated dicarboxylic acids, amides of  
15 unsaturated anhydrides, salts of unsaturated monocarboxylic acids, salts of unsaturated dicarboxylic acids, salts of unsaturated anhydrides, unsaturated hydrocarbons, unsaturated heterocycles, and mixtures thereof.

More preferred monomer units are selected from the group consisting of acrylic acid, methacrylic acid, N,N-dimethyl acrylamide, dimethylaminoethyl methacrylate, quaternized  
20 dimethylaminoethyl methacrylate, vinyl pyrrolidone, C<sub>1</sub>-C<sub>18</sub> alkyl esters of acrylic or methacrylic acid, styrene, alpha-methylstyrene, t-butylstyrene, vinyl acetate, vinyl propionate, vinyl chloride, vinylidene chloride, vinyl toluene, 2-methoxyethyl acrylate, n-butyl methacrylate, isobutyl methacrylate, t-butyl acrylate, t-butyl methacrylate, 2-ethylhexyl methacrylate, methyl methacrylate, salts of any acids and amines listed above, and  
25 combinations thereof.

Most preferred monomer units of said backbone (i) selected from the group consisting of acrylic acid, methacrylic acid, 2-methoxyethyl acrylate, n-butyl methacrylate, isobutyl methacrylate, t-butyl acrylate, t-butyl methacrylate, 2-ethylhexyl methacrylate, methyl methacrylate and mixtures thereof..

30 The backbone has a Tg of from about 0° C to about 45° C, preferably from about 0° C to about 35° C, and most preferably from about 0° C to about 25° C.

#### Acrylic and Methacrylic Acid Macromonomer Side Chain Units

The copolymers of the present invention comprise from about 2% to about 50%, preferably from about 5% to about 40%, and more preferably from about 10% to about 30%,  
35 by weight of the copolymer of acrylic and methacrylic macromonomer side chain units.

The macromonomer units are copolymerizable with the vinyl monomers, said macromonomers preferably having a vinyl moiety. Either a single type of macromonomer

unit or combinations of two or more macromonomer units can be utilized herein. The macromonomers are selected to meet the requirements of the copolymer. By "copolymerizable", as used herein, is meant that the macromonomers can be reacted with or polymerized with the vinyl monomers in a polymerization reaction using one or more conventional synthetic techniques, as described above.

The macromonomers that are useful herein contain a polymeric portion and a copolymerizable moiety which is preferably an ethylenically unsaturated moiety. Typically, the preferred macromonomers are those that are endcapped with the vinyl moiety. By "endcapped" as used herein is meant that the vinyl moiety is at or near a terminal position of the macromonomer.

The macromonomers can be synthesized utilizing a variety of standard synthetic procedures familiar to the polymer chemist of ordinary skill in the art. Furthermore, these macromonomers can be synthesized starting from commercially-available polymers. Typically, the weight average molecular weight of the macromonomer is from about 1000 to about 50,000.

Preferred macromonomers are poly(acrylate) and polymethacrylate) macromonomers. Macromonomers are exemplified by the general formula:



wherein I is an optionally present initiator (i.e. n = 0 or 1), W is a monomer unit, E is an endcapping group, and m is an integer from about 10 to about 2000.

I is an optionally present chemical initiator moiety. Without being limited by theory, I can be derived from a chemical initiator or solvent used in the synthesis of the macromonomer. Nonlimiting examples of such initiators from which I can be derived include hydrogen ion, hydrogen radical, hydride ion, hydroxide ion, hydroxyl radical, peroxide radical, peroxide anion, C<sub>1</sub>-C<sub>20</sub> carbocations, C<sub>1</sub>-C<sub>20</sub> carbanions, C<sub>1</sub>-C<sub>20</sub> carbon radicals, C<sub>1</sub>-C<sub>20</sub> aliphatic and aromatic alkoxy anions, ammonium ion, and substituted ammonium ions (e.g., C<sub>1</sub>-C<sub>20</sub> alkyl and C<sub>1</sub>-C<sub>20</sub> alkoxy substituted), and mixtures thereof. I can be derived from any useful solvent, nonlimiting examples of which include water, methanol, ethanol, propanol, isopropanol, acetone, hexane, dichloromethane, chloroform, benzene, toluene, and mixtures thereof.

W is selected from the group consisting of an acrylic acid monomer unit, a methacrylic acid monomer unit and mixtures thereof. Nonlimiting classes of such monomers include C<sub>1</sub>-C<sub>18</sub> straight and branched chain acrylate esters and C<sub>1</sub>-C<sub>18</sub> straight and branched chain methacrylate esters, and mixtures thereof.

Preferably the monomer units of the side chains are selected from the group consisting of acrylic acid (produced by hydrolysis of trimethylsilyl acrylate), methacrylic acid (produced by hydrolysis of trimethylsilyl methacrylate), phenyl methacrylate, benzyl

methacrylate, and C<sub>1</sub>-C<sub>18</sub> alkyl esters of acrylic or methacrylic acid and mixtures thereof. More preferably, the monomer units are selected from the group consisting acrylic acid (preferably produced by hydrolysis of trimethylsilyl acrylate), methacrylic acid (preferably produced by hydrolysis of trimethylsilyl acrylate), n-propyl methacrylate, iso-butyl methacrylate, tert-butyl acrylate, tert-butyl methacrylate, 2-hydroxyethyl methacrylate (produced by hydrolysis of trimethylsilyl protected alcohol), 2-hydroxypropyl methacrylate (produced by hydrolysis of trimethylsilyl protected alcohol). Most preferred are monomer units of selected from the group consisting of acrylic acid (preferably produced by hydrolysis of trimethylsilyl acrylate), methacrylic acid (preferably produced by hydrolysis of trimethylsilyl methacrylate), n-propyl methacrylate, iso-butyl methacrylate and mixtures thereof.

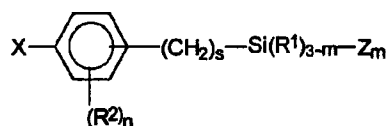
Each side chain has a T<sub>g</sub> of from about 50°C to about 200°C, preferably of from about 60°C to about 150°C and most preferably of from about 70°C to about 110°C.

Optionally, the adhesive copolymers can further comprise one or more polysiloxane macromonomer side chains exemplified by the general formula:

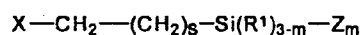


wherein X is a vinyl group copolymerizable with the vinyl monomer units; Y is a divalent linking group; each R is independently selected from the group consisting of hydrogen, hydroxyl, C<sub>1</sub>-C<sub>6</sub> alkyl, C<sub>1</sub>-C<sub>6</sub> alkoxy, C<sub>2</sub>-C<sub>6</sub> alkylamino, phenyl, C<sub>1</sub>-C<sub>6</sub> alkyl or alkoxy-substituted phenyl; Z is a monovalent siloxane polymeric moiety having a number average molecular weight of at least about 1000, is essentially unreactive under copolymerization conditions, and is pendant from the vinyl polymeric backbone described above; n is 0 or 1; and m is an integer from 1 to 3. The polysiloxane macromonomer has a weight average molecular weight from about 1000 to about 50,000, preferably from about 5,000 to about 30,000, more preferably from about 8,000 to about 25,000.

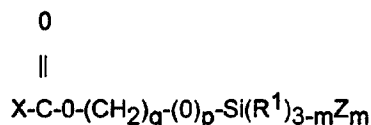
Preferably, the polysiloxane macromonomer has a formula selected from the following formulas:



or



or

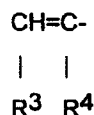


In these structures s is an integer from 0 to 6; preferably 0, 1, or 2; more preferably 0 or 1; m is an integer from 1 to 3, preferably 1; p is 0 or 1; q is an integer from 2 to 6; each R<sup>1</sup> is

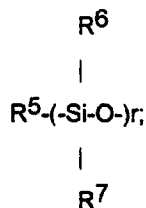


independently selected from the group consisting of hydrogen, hydroxyl, C1-C6 alkyl, C1-C6 alkoxy, C2-C6 alkylamino, phenyl, C1-C6 alkyl or alkoxy-substituted phenyl, preferably C1-C6 alkyl, or C1-C6 alkyl or alkoxy-substituted phenyl, more preferably C1-C6 alkyl, even more preferably methyl, R<sup>2</sup> is selected from the group consisting of C1-C6 alkyl or C1-C6 alkyl substituted phenyl, preferably methyl.

n is an integer from 0 to 4, preferably 0 or 1, more preferably 0; X is



wherein R<sup>3</sup> is hydrogen or -COOH, preferably R<sup>3</sup> is hydrogen; R<sup>4</sup> is hydrogen, methyl or -CH<sub>2</sub>COOH, preferably R<sup>4</sup> is methyl; Z is



wherein R<sup>5</sup>, R<sup>6</sup>, and R<sup>7</sup>, are independently selected from hydrogen, hydroxyl, C1-C6 alkyl, C1-C6 alkoxy, C2-C6 alkylamino, phenyl, C1-C6 alkyl or alkoxy-substituted phenyl, hydrogen or hydroxyl, preferably R<sup>5</sup>, R<sup>6</sup>, and R<sup>7</sup> are C1-C6 alkyls; more preferably methyl; and r is an integer of from about 14 to about 700, preferably about 60 to about 400, and more preferably about 100 to about 350.

Exemplary grafted polymers for use in the present invention include the following, where the composition is given as weight part of monomer used in the synthesis:

- (i) poly(t-butyl acrylate-co-2-methoxyethyl acrylate-co-methacrylic acid)-graft-poly (n-propyl methacrylate-co-methacrylic acid)  
 MWt of copolymer: 149,900  
 Backbone: 80 %  
 Backbone Composition: t-butyl acrylate (53%), 2-methoxyethyl acrylate (36%), methacrylic acid (11%)  
 Macromonomer side chains: 20%  
 Macromonomer side chains Composition: n-propyl methacrylate (65%); methacrylic acid (35%)  
 Macromonomer side chains MWt: 6,000
- (ii) poly(t-butyl acrylate-co-2-methoxyethyl acrylate-co-methacrylic acid)-graft-poly (iso-butyl methacrylate-co-methacrylic acid)  
 MWt of copolymer: 55,000  
 Backbone: 80 %

- Backbone Composition: t-butyl acrylate (53%), 2-methoxyethyl acrylate (36%), methacrylic acid (11%)  
 Macromonomer side chains: 20%  
 Macromonomer side chains Composition: iso-butyl methacrylate (65%); methacrylic acid (35%)  
 MWt of Macromonomer side chains: 8,000
- (iii) poly(t-butyl acrylate-co-2-methoxyethyl acrylate-co-acrylic acid)-graft-[poly(n-propyl methacrylate-co-methacrylic acid); poly(dimethylsiloxane)]  
 MWt of copolymer: 83,000
- Backbone: 77 %  
 Backbone Composition: t-butyl acrylate (43%), 2-methoxyethyl acrylate (38%), acrylic acid (18%)  
 Macromonomer side chains: 17%  
 Macromonomer side chains Composition: n-propyl methacrylate (60%); methacrylic acid (40%)  
 MWt of Macromonomer side chains: 6,000  
 Poly(dimethylsiloxane) macromonomer side chains: 6%  
 MWt of poly(dimethylsiloxane): 10,000
- (iii) poly(t-butyl acrylate-co-2-methoxyethyl acrylate-co-acrylic acid)-graft-[poly(n-propyl methacrylate-co-methacrylic acid); poly(dimethylsiloxane)]  
 MWt of copolymer: 150,000  
 Backbone: 77 %  
 Backbone Composition: t-butyl acrylate (43%), 2-methoxyethyl acrylate (38%), acrylic acid (18%)  
 Macromonomer side chains: 20%  
 Macromonomer side chains Composition: n-propyl methacrylate (60%); methacrylic acid (40%)  
 MWt of Macromonomer side chains: 10,000  
 Poly(dimethylsiloxane) macromonomer side chains: 3%  
 MWt of poly(dimethylsiloxane): 10,000

The copolymers of the present invention are prepared by the polymerization combination of vinyl monomers and macromonomers. The copolymers can be synthesized by free radical polymerization of the monomers and macromonomers. The general principles of free radical polymerization methods are well understood. See, for example, Odian, "Principles of Polymerization", 3rd edition, John Wiley & Sons, 1991, pp. 198-334, incorporated by reference herein. The desired vinyl monomers and macromonomers are all placed in a reactor, along with a sufficient amount of a mutual solvent so that when the

reaction is complete the viscosity of the reaction is reasonable. Undesired terminators, especially oxygen, are removed as needed. This can be done by evacuation or by purging with an inert gas, such as argon or nitrogen. The initiator is introduced and the reaction brought to the temperature needed for initiation to occur, assuming thermal initiators are used. Alternatively, redox or radiation initiation can be used. The polymerization is allowed to proceed as long as needed for a high level of conversion to be achieved, typically from a few hours to a few days. The solvent is then removed, usually by evaporation or by precipitating the copolymer by addition of a nonsolvent. The copolymer can be further purified, as desired.

As an alternative to a batch reaction, the copolymer can be made by a semi-continuous or continuous process. In the semi-continuous process, two or more additions of monomers or macromonomers are made during the polymerization reaction. This is advantageous when the copolymer is made of several monomers which react during the polymerization at different rates. The proportions of monomers added to the reaction at the separate points of addition can be adjusted by one of ordinary skill in the art such that the polymers of the final product have a more uniform structure. In other words, the polymers of the final product will have a more consistent monomer content distribution for each of the monomer types charged to the reaction.

The copolymers are prepared by the polymerization combination of vinyl monomers and macromonomers. The copolymer composition is characterized by the amount of each monomer charged to the polymerization reaction vessel, or alternatively used in a continuous or semi-continuous process.

By appropriate selection and combination of the particular vinyl monomer units and macromonomer units, and by the choice of specific relative ratios of the units well within the ability of one of ordinary skill in the art, the copolymers can be optimized for various physical properties and for compatibility with other ingredients commonly used in hair care applications.

As is be clear to one skilled in the art, the copolymer may have one or more side chains grafted to the backbone. In addition, the polymers of the present invention can be used alone or in addition to the copolymer, low levels of the corresponding copolymers having no side chains grafted to the backbone. As known in the art, synthetic graft copolymerization processes may produce a mixture of polymer molecules containing none, one, or more than one side chains covalently bonded to and pendant from the polymeric backbone. From knowledge of the amount and number average molecular weight of side chains in a polymer sample, and the number average molecular weight of the polymer sample, it is possible to calculate the average number of side chains per polymer backbone.

#### Optional Components

The copolymers of the present invention can be formulated into personal care compositions, or any other composition in which an adhesive polymer may be useful such as adhesive tapes, glues, and the like. Personal care compositions comprise from about 0.1% to about 99%, preferably from 0.5% to about 50%, more preferably from about 1% to about 10%, by weight of the composition, of the grafted polymer and from about 0.1% to about 99.9%, preferably from about 0.5% to about 99.0% and most preferably from about 1.0% to about 99.9% of a suitable personal care carrier. Solvents are preferably selected from the group consisting of water, ethanol, *n*-propanol, isopropanol, and mixtures thereof. The polymers are soluble at a concentration of at least about 0.1 mg/mL, preferably at least about 0.5 mg/mL, and more preferably at least about 1 mg/mL, at about 25°C.

The graft polymers made in accordance with the synthesis methods herein may have acidic functionalities, such as carboxyl groups, and are usually used in at least partially neutralized form to promote solubility/dispersability of the polymer. In addition, use of the neutralized form aids in the ability of the hair styling compositions to be removed from the hair by shampooing. The extent of such neutralization ranges from about 10% to 100%, more preferably from about 20% to about 90%, even more preferably from about 40% to about 85%, neutralization of the acidic functionalities of the graft polymer.

Neutralization of the graft polymers containing acidic functionalities may be accomplished by any conventional or otherwise known technique for effecting such neutralization of by using an organic or inorganic base material. Metallic bases are particularly useful for this purpose. Suitable base neutralizers include, but are not limited to, ammonium hydroxides, alkali metal hydroxides, or an alkaline earth metal hydroxides, preferably potassium hydroxide and sodium hydroxide. Examples of other suitable neutralizing agents include, but are not limited to, amines or amino alcohols such as 2-amino-2-methyl-1,3-propanediol (AMPD), 2-amino-2-ethyl-1,3-propanediol (AEPD), 2-amino-2-methyl-1-propanol (AMP), 2-amino-1-butanol (AB), monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA), monoisopropanolamine (MIPA), diisopropanolamine (DIPA), triisopropanolamine (TIPA) and dimethyl stearamine (DMS). Preferred are amines and metallic bases.

Neutralization of graft polymers containing basic functionalities, e.g., amino groups, are likewise preferably at least partially neutralized with an organic or inorganic acid e.g., hydrogen chloride. Neutralization can be accomplished by any conventional or otherwise known technique for accomplishing such neutralization. The preferred extent of neutralization is the same as that described for neutralization of acidic functionalities. Solubility for any neutralized graft polymers made in accordance with the method herein should be determined only after the desired acid or base neutralization.

The solvents that are present in hair care compositions are at a level of from about 80% to about 99%, preferably from about 85% to about 98%, more preferably from about 90% to about 95% of the total composition.

5 The solvents essential to such compositions are selected from the group consisting of water, C<sub>2</sub>-C<sub>3</sub> monohydric alkanols, and mixtures thereof. If present, C<sub>3</sub> alkanols, such as isopropanol, should be used at levels no greater than about 15% by weight of the composition, preferably no greater than about 12%, more preferably no greater than about 10%. High levels of C<sub>3</sub> monohydric alcohols are undesirable in the present compositions due to potential odor issues they can create. Preferred polar solvent phases contain water,  
10 ethanol, or mixtures thereof.

Where water and alcohol mixtures are used, for instance, water-ethanol or water-isopropanol-ethanol, the water content of the compositions is generally in the range of from about 0.5% to about 99%, preferably from about 5% to about 50% by weight of the total composition. In such mixtures, the alcohol solvents are generally present in the range of  
15 from 0.5% to about 99%, preferably from about 50% to about 95%, by weight of the total composition.

In yet another aspect of this invention are provided hair styling products, such as hair spray compositions, which contain reduced levels of volatile organic solvents. A reduced volatile organic solvent hair spray composition of the present invention contains no  
20 more than 80% volatile organic solvents (which include, for example, alkanols but not water). As used herein, volatile organic solvents means solvents which have at least one carbon atom and exhibit a vapor pressure of greater than 0.1 mm Hg at 20°C.

In reduced volatile organic solvent hair styling products, the compositions generally comprise at least 10%, by weight, of water. It is also specifically contemplated that they  
25 may contain at least about 11%, 12%, 13%, 14%, 15%, or more water.

The reduced volatile organic solvent compositions hereof will comprise up to about 90%, preferably up to about 70%, more preferably up to about 60% even more preferably no more than about 50%, water; and from about 10% to about 80%, preferably from about 20% to about 80%, more preferably from about 40% to about 80%, of volatile organic solvent. It is  
30 also contemplated that the compositions can be limited to containing no more than about 75%, 65%, 55%, or other levels of volatile organic solvents.

In addition the compositions could contain branched chain hydrocarbon solvent present at a level of from about 0.1% to about 15%, preferably from about 0.5% to about 10%, more preferably from about 2% to about 8%, by weight of the composition. Also useful  
35 are low boiling point silicone oils.

The branched chain hydrocarbon solvent is characterized by a boiling point of at least about 105°C, preferably at least about 110°C, more preferably at least about 125°C,

most preferably at least about 150°C. The boiling point is also generally about 260°C or less, preferably about 200°C or less. The hydrocarbon chosen should also be safe for topical application to the hair and skin.

The branched chain hydrocarbon solvents are selected from the group consisting of  
5 C<sub>10</sub>-C<sub>14</sub> branched chain hydrocarbons, and mixtures thereof, preferably C<sub>11</sub>-C<sub>13</sub> branched chain hydrocarbons, more preferably C<sub>12</sub> branched chain hydrocarbons. Saturated hydrocarbons are preferred, although it is not necessarily intended to exclude unsaturated hydrocarbons.

Examples of suitable nonpolar solvents include isoparaffins of the above chain  
10 sizes. Isoparaffins are commercially available from Exxon Chemical Co. Examples include Isopar™ G (C<sub>10</sub>-C<sub>11</sub> isoparaffins), Isopar™ H and K (C<sub>11</sub>-C<sub>12</sub> isoparaffins), and Isopar™ L (C<sub>11</sub>-C<sub>13</sub> isoparaffins). The most preferred nonpolar solvent are C<sub>12</sub> branched chain hydrocarbons, especially isododecane. Isododecane is commercially available from Preperse, Inc. (South Plainfield, NJ, USA) as Permethyl™ 99A.

15 Plasticizer

The compositions hereof can optionally contain a plasticizer for the grafted polymer. Any plasticizer suitable for use in hair care products or for topical application to the hair or skin can be used. A wide variety of plasticizers are known in the art. These include acetyl triethylcitrate, triethylcitrate, glycerin, diisobutyl adipate, butyl stearate, and propylene glycol.  
20 Plasticizers are typically used at levels of from about 0.01% to about 10%, by weight of the composition, preferably from about 0.05% to about 3%, more preferably from about 0.05% to about 1%.

Additional Adhesive Polymer

The adhesive polymers of the present invention can be used in combination with an  
25 additional adhesive polymer. The compositions hereof will generally comprise from about 0.1% to about 15%, preferably from 0.5% to about 8%, more preferably from about 1% to about 8%, by weight of the composition, of the adhesive polymer. It is not intended to exclude the use of higher or lower levels of the polymers, as long as an effective amount is used to provide adhesive or film-forming properties to the composition and the composition  
30 can be formulated and effectively applied for its intended purpose. By adhesive polymer what is meant is that when applied as a solution to a surface and dried, the polymer forms a film. Such a film will have adhesive and cohesive strength, as is understood by those skilled in the art.

The polymeric backbone is chosen such that it is compatible with the adhesive  
35 styling polymer. By "compatible" is meant is that, when placed in a suitable solvent, the polymers form a stable solution, i. e., the polymers do not compete for solubility and therefore, cause no phase separation and when the solution is dried a uniform film is formed,

with no macrophase separation of the two polymers. A suitable solvent is a solvent which substantially completely dissolves the non-silicone and silicone grafted polymers at the levels described herein. The polymer blend forms a relatively clear hairspray system (% transmittance at 450 nm is generally greater than 80%). It is recognized that certain plasticizers can form cloudy films as well as incorrect neutralization levels. Therefore, this would fall outside this definition of compatibility. The compatibility can be tested by dissolving the polymers in a mutual solvent, and then evaporating the solvent to form a film. Incompatible polymers will form a cloudy film with poor mechanical properties, due to the large scale phase separation of the two polymers. Although compatibility can occur between two polymers of completely different structures, it is preferred that compatibility be obtained by making the composition of the respective backbones similar to or identical to one another.

The adhesive polymer should have a weight average molecular weight of at least about 20,000, preferably greater than about 25,000, more preferably greater than about 30,000, most preferably greater than about 35,000. There is no upper limit for molecular weight except that which limits applicability of the invention for practical reasons, such as processing, aesthetic characteristics, formulateability, etc. In general, the weight average molecular weight will be less than about 10,000,000, more generally less than about 5,000,000, and typically less than about 2,000,000. Preferably, the weight average molecular weight will be between about 20,000 and about 2,000,000, more preferably between about 30,000 and about 1,000,000, and most preferably between about 40,000 and about 500,000.

Preferably the weight ratio of the toughened graft polymer of the present invention to adhesive polymer ranges from about 1:10 to about 1:1, preferably from about 1:5 to about 1:1.

Exemplary adhesive polymers for use in the present invention include the following, where the numbers following the structure indicate the weight ratios of monomers as loaded into the polymerization reactor:

- (i) acrylic acid/t-butyl acrylate 25/75
- (ii) dimethylaminoethyl methacrylate/isobutyl methacrylate/2-ethylhexyl-methacrylate 40/40/20
- (iii) t-butylacrylate/acrylic acid 65/35
- (iv) polymer (ii) quaternized by treatment with methyl chloride

The adhesive polymers can be synthesized as described above such as by free radical polymerization of the monomers.

Solubility of the adhesive polymer, as described above, should be determined after neutralization, if any, as well as after addition of other ingredients that may be included in the polar solvent phase, such as surfactants, solubilizers, etc.

The present compositions can contain a wide variety of additional optional ingredients, including among them any of the types of ingredients known in the art for use in hair setting compositions, especially hair spray compositions and hair setting tonics. These ingredients include, but are not limited to, surfactants (including fluorinated surfactants and  
5 silicone copolyols), and ionic strength modifiers, propellants, hair conditioning agents (e.g., silicone fluids, fatty esters, fatty alcohols, long chain hydrocarbons, cationic surfactants, etc.)

#### Ionic Strength Modifier System

Optionally, the compositions can contain an effective amount of a non-surface  
10 active ionic strength modifier system for reducing the viscosity of the hair spray composition. When used, the ionic strength modifiers will be present in the present compositions at a level of at least about 0.01%, by weight of the composition. The upper limit is dependent upon the maximum amount of the ionic strength modifiers that can be present in the particular compositions hereof such that the hair setting resin remains solubilized or  
15 dispersed. As will be understood by those skilled in the art, as the ionic strength of the composition is increased, the resin will eventually fall out of solution, or otherwise no longer remain solubilized or dispersed in the polar liquid carrier. The upper limit of the ionic strength modifier system level will vary depending upon the particular ionic strength modifiers, liquid vehicle, resin, and other ingredients present in the composition. Thus, for  
20 example, the maximum amount of the ionic strength modifiers that can be used will tend to be lower for compositions with liquid vehicles containing less water, compared to compositions with more water. Generally, the compositions will comprise about 4%, by weight, or less of the ionic strength modifiers, more generally about 2% or less, and typically about 1% or less. Preferably, the compositions hereof will comprise from about 0.01% to about 0.5%,  
25 more preferably from about 0.01% to about 0.1%, of the ionic strength modifier system.

The ionic strength modifier system comprises a mixture of monomeric cations and anions. The ions of the ionic strength modifier system hereof are non-surface active, i.e. they do not significantly reduce surface tension. For purposes hereof, non-surface active shall mean the ions, which at a 0.5% aqueous solution concentration, reduce surface  
30 tension by no more than 5.0 dynes/cm<sup>2</sup>. Generally, the ions of the ionic strength modifier system hereof will be characterized by having, at maximum, four or less carbon atoms per charge, preferably two or less carbon atoms, in any aliphatic chain or straight or branched chain organic heterochain.

The ionic strength modifier system comprises monomeric ions of the type which are  
35 products of acid-base reactions. Thus, basic and acidic ions OH<sup>-</sup> and H<sup>+</sup> do not constitute part of the ionic strength modifier system hereof, although they may be present in the composition. The ions hereof are incorporated into the composition in a form such that they



can exist in the composition as free ions, i.e., in dissociated form. It is not necessary that all of the ions added exist in the composition as free ions, but must be at least partially soluble or dissociated in the composition. The ionic strength modifiers can be incorporated into the hair styling compositions, for example, by addition of soluble salts, or by addition of mixtures of acids and bases, or by a combination thereof. It is a necessary aspect of the invention that both anions and cations of the ionic strength modifier system be included in the composition.

Suitable cations for use include, for example, alkali metals, such as lithium, sodium, and potassium, and alkaline-earth metals, such as magnesium, calcium, and strontium. Preferred of the divalent cations is magnesium. Preferred monovalent metal ions are lithium, sodium, and potassium, particularly sodium and potassium. Suitable means of addition to the compositions hereof include, for example, addition as bases, e.g., hydroxides, sodium hydroxide and potassium hydroxide, and such as salts that are soluble in the liquid carrier, e.g. salts of monomeric anions such as those described below.

Other suitable cations include organic ions, such as quaternary ammonium ions and cationic amines, such as ammonium mono-, di-, and tri-ethanolamines, triethylamine, morpholine, aminomethylpropanol (AMP), aminoethylpropanediol, etc. Ammonium and the amines are preferably provided in the forms of salts, such as hydrochloride salts.

Monomeric anions that can be used include halogen ions, such as chloride, fluoride, bromide, and iodide, particularly chloride, sulfate, ethyl sulfate, methyl sulfate, cyclohexyl sulfamate, thiosulfate, toluene sulfonate, xylene sulfonate, citrate, nitrate, bicarbonate, adipate, succinate, saccharinate, benzoate, lactate, borate, isethionate, tartrate, and other monomeric anions that can exist in dissociated form in the hair styling composition. The anions can be added to the compositions hereof, for example, in the form of acids or salts which are at least partially soluble in the liquid vehicle, e.g., sodium or potassium salts of acetate, citrate, nitrate, chloride, sulfate, etc. Preferably, such salts are entirely soluble in the vehicle.

The use of ionic strength modifiers are especially useful in reduced volatile organic solvent compositions, most especially those utilizing silicone macromer-containing polymers.

#### Personal Care Compositions

The adhesive polymers of the present invention can be used in a wide variety of personal care compositions, including shampoos, soaps, lotions, creams, antiperspirants, nail enamels, lipsticks, foundations, mascaras, sunscreens, hair spray compositions, mousses, and hair setting tonics. Compositions that will be flowable, e.g., low viscosity

compositions that, preferably, are suitable for spray application as well as higher viscosity compositions are also contemplated.

Personal care carriers are suitable for use in the present invention are described in U.S. Patent 5,306,485 to Robinson et al., issued April 26, 1994, and U.S. Patent 5,002,680 to Schmidt et al., issued March 26, 1991, both of which are incorporated by reference  
5 herein. Hair spray compositions and mousses of the present invention can be dispensed from containers which are aerosol dispensers or pump spray dispensers. Such dispensers, i.e., containers, are well known to those skilled in the art and are commercially available from a variety of manufacturers, including American National Can Corp. and Continental  
10 Can Corp.

When the hair spray compositions are to be dispensed from a pressurized aerosol container, a propellant which consists of one or more of the conventionally-known aerosol propellants may be used to propel the compositions. A suitable propellant for use can be generally any liquifiable gas conventionally used for aerosol containers.

15 Suitable propellants for use are volatile hydrocarbon propellants which can include liquefied lower hydrocarbons of 3 to 4 carbon atoms such as propane, butane and isobutane. Other suitable propellants are hydrofluorocarbons such as 1,2-difluoroethane (Hydrofluorocarbon 152A) supplied as Dymel 152A by DuPont. Other examples of propellants are dimethylether, N-butane, isobutane, propanes, nitrogen, carbon dioxide,  
20 nitrous oxide and atmospheric gas and mixtures thereof.

The aerosol propellant may be mixed with the present compositions and the amount of propellant to be mixed is governed by normal factors well known in the aerosol art. Generally, for liquifiable propellants, the level of propellant is from about 10% to about 60% by weight of the total composition, preferably from about 15% to about 40% by weight of the  
25 total composition.

Alternatively, pressurized aerosol dispensers can be used where the propellant is separated from contact with the hair spray composition such as a two compartment can of the type sold under the tradename SEPRO from American National Can Corp.

Other suitable aerosol dispensers are those characterized by the propellant being  
30 compressed air which can be filled into the dispenser by means of a pump or equivalent device prior to use. Such dispensers are described in U.S. Patents 4,077,441, March 7, 1978, Olofsson and 4,850,577, July 25, 1989, TerStegge, both incorporated by reference herein, and in U.S. Serial No. 07/839,648, Gosselin et al., filed February 21, 1992, also incorporated by reference herein. Compressed air aerosol containers suitable for use are  
35 also currently marketed by The Procter & Gamble Company under their tradename VIDAL SASSOON AIRSPRAY® hair sprays.

Conventional non-aerosol pump spray dispensers, i.e., atomizers, can also be used.

Other hair styling compositions include tonics and lotions, which are typically dispensed in a conventional bottle or tube, and applied directly to the hair or first dispensed to the hand and then to the hair.

5 The hair styling formulations of the present invention can optionally contain conventional hair care composition adjuvants. Generally, adjuvants collectively can  
comprise from about 0.05% to about 5% by weight and preferably from about 0.1% to about  
3%, by weight. Such conventional optional adjuvants are well known to those skilled in the  
art and include in addition to those discussed above, emollients; lubricants and penetrants  
10 such as various lanolin compounds; protein hydrolysates and other protein derivatives; ethylene adducts and polyoxyethylene cholesterol; dyes, tints, bleaches, reducing agents  
and other colorants; pH adjusting agents sunscreens; preservatives; thickening agents (e.g.  
polymeric thickeners, such as xanthan gum); and perfume.

The personal care compositions of the present invention can be made using conventional formulation and mixing techniques.

15 The compositions of the present invention are used in conventional ways to provide the personal care compositions of the present invention. Such method generally involves application of an effective amount of the product. For example, in a hair spray composition, said composition is applied to the desired dry, slightly damp, or wet hair before and/or after the hair is arranged to a desired style. The composition is then dried or allowed to dry. By  
20 "effective amount" is meant an amount sufficient to provide the desired benefits.

The following Examples further illustrate embodiments within the scope of the present invention. They are given solely for the purposes of illustration and are not to be construed as limitations of the present invention as many variations of the invention are possible without departing from its spirit and scope.

#### 25 EXAMPLES

The following synthesis exemplify grafted polymers useful in the present compositions.

##### Synthesis of para-vinyl benzoyl chloride

To a clean round bottom flask with an argon atmosphere and equipped with a magnetic stir  
30 bar is added para-vinyl benzoic acid (10 g, 0.067 mole) which is suspended in benzene (25 ml). Oxalyl chloride (25 g, 0.197 mole) is added to the flask. The mixture is stirred for 8 hours and continuously flushed with a continuous stream of argon to purge the system of the gases generated during the reaction. Solvent and excess oxalyl chloride is stripped off under vacuum. Finally, the product is distilled under vacuum to yield para-vinyl benzoyl chloride.  
35 Approximately 90% of the theoretical yield is obtained.

##### Synthesis of Vinylphenyl-terminated Poly(n-propyl methacrylate-co-methacrylic acid) Macromonomer

Into a round-bottomed-flask fitted with a magnetic stirring and under slight argon pressure (8 psi), is added tetrahydrofuran (1L), trimethylsilylmethacrylate (100g, 0.632 mole), and n-propylmethacrylate (100g, 0.780 mole). The solution is cooled to -80°C then initiated with diphenylhexyllithium (0.0275 moles) (prepared by adding 1:1 mole ratio of sec-butyl lithium and 1,1-diphenyl ethylene in THF) for chain propagation via anionic polymerization mechanism. After continuous stirring for 0.5 hours, vinylbenzoyl chloride (8.33 mL, 0.05 mole) is charged to the solution and continued stirring for 0.5 hours. The solution is then warmed to ambient temperature and H<sub>2</sub>O (10mL) is added and stirred for 0.25 hours to deprotect the acid groups. The macromonomer, which has a weight average molecular weight of about 6000, is obtained by precipitating the resulting solution in hexanes, collecting precipitate, and drying under vacuum.

#### Example 1

Synthesis of Poly(t-butylacrylate-co-2-methoxyethylacrylate-co-acrylic acid)-graft-[poly(n-propyl methacrylate-co-methacrylic Acid);poly(dimethylsiloxane)] Copolymer

To a round-bottomed-flask equipped with a reflux condenser, temperature control, mechanical stirring mechanism, and under slight argon pressure (8psi), is added acetone (0.5L), t-butylacrylate (22.3g), 2-methoxyethylacrylate (36g), acrylic acid (18g), poly(dimethylsiloxane) macromonomer (6g) (Chisso Corp. Tokyo, Japan), and vinylphenyl-terminated (n-propylmethacrylate-co-methacrylic acid) macromonomer (18g) (from Example 2). Solution is stirred until all components are dissolved, then heated to 60°C. Azobisisobutyronitrile (0.7g) is charged to the system. After 10 hours, solution is cooled and precipitated in water to yield silicone modified graft copolymer.

#### Example 2

Synthesis of Poly(t-butylacrylate-co-2-methoxyethylacrylate-co-methacrylic acid)-graft-[poly(n-propyl methacrylate-co-methacrylic Acid) Copolymer

To a round-bottomed-flask equipped with a reflux condenser, temperature control, mechanical stirring mechanism, and under slight argon pressure (8psi), is added acetone (0.5L), t-butylacrylate (42.4 g), 2-methoxyethyl acrylate (29g), methacrylic acid (9g), and vinylphenyl-terminated (n-propylmethacrylate-co-methacrylic acid) macromonomer (20g) (from Example 2). Solution is stirred until all components are dissolved, then heated to 60°C. Azobisisobutyronitrile (0.5g) is charged to the system. After 10 hours, solution is cooled and precipitated in water to yield the graft copolymer.

## CLAIMS:

1. An adhesive copolymer, said copolymer being characterized by an organic polymeric backbone wherein said backbone has a Tg of from 0°C to 45°C wherein said copolymer comprises one or more side chains grafted thereon consisting of acrylic and methacrylic monomer units wherein [each of] said side chains have a Tg of greater than 50°C -200°C wherein the number average molecular weight of said side chain is greater than 1000.
2. An adhesive copolymer according to claim 1, wherein said backbone monomer unit is selected from the group consisting of unsaturated alcohols, unsaturated monocarboxylic acids, unsaturated dicarboxylic acids, unsaturated anhydrides, alcohol esters of unsaturated monocarboxylic acids, alcohol esters of unsaturated dicarboxylic acids, alcohol esters of unsaturated anhydrides, alkoxyated esters of unsaturated monocarboxylic acids, alkoxyated esters of unsaturated dicarboxylic acids, alkoxyated esters of unsaturated anhydrides, aminoalkyl esters of unsaturated monocarboxylic acids, aminoalkyl esters of unsaturated dicarboxylic acids, aminoalkyl esters of unsaturated anhydrides, amides of unsaturated monocarboxylic acids, amides of unsaturated dicarboxylic acids, amides of unsaturated anhydrides, salts of unsaturated monocarboxylic acids, salts of unsaturated dicarboxylic acids, salts of unsaturated anhydrides, unsaturated hydrocarbons, unsaturated heterocycles, and mixtures thereof.
3. An adhesive copolymer according to claim 2, wherein said backbone monomer unit is selected from the group consisting of acrylic acid, methacrylic acid, N,N-dimethyl acrylamide, dimethylaminoethyl methacrylate, quaternized dimethylaminoethyl methacrylate, vinyl pyrrolidone, C<sub>1</sub>-C<sub>18</sub> alkyl esters of acrylic or methacrylic acid, styrene, alpha-methylstyrene, t-butylstyrene, vinyl acetate, vinyl propionate, vinyl chloride, vinylidene chloride, vinyl toluene, 2-methoxyethyl acrylate, n-butyl methacrylate, isobutyl methacrylate, t-butyl acrylate, t-butyl methacrylate, 2-ethylhexyl methacrylate, methyl methacrylate, salts of any acids and amines listed above, and combinations thereof, wherein the backbone of has a Tg of from 0° C to 45° C,
4. An adhesive copolymer according to claim 1, wherein said side chain has general formula:

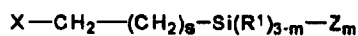
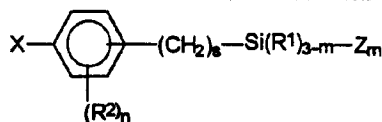


wherein I is an initiator,  $n = 0$  or  $1$ , W is a monomer unit from the group consisting of an acrylic acid monomer unit, a methacrylic acid monomer unit and mixtures thereof, E is an endcapping group, and  $m$  is an integer from 10 to 2000.

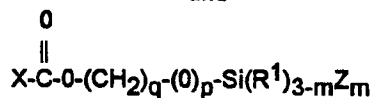
5. A personal care composition according to claim 4, wherein said monomer unit of said side chain is selected from the group consisting of an acrylic acid monomer unit, a methacrylic acid monomer unit and mixtures thereof. Nonlimiting classes of such monomers include  $C_1$ - $C_{18}$  straight and branched chain acrylate esters and  $C_1$ - $C_{18}$  straight and branched chain methacrylate esters, and mixtures thereof.
6. A personal care composition according to claim 5, wherein said monomer unit of each of said side chains is selected from the monomer units are selected from the group consisting acrylic acid, methacrylic acid, n-propyl methacrylate, iso-butyl methacrylate, tert-butyl acrylate, tert-butyl methacrylate, 2-hydroxyethyl methacrylate, 2-hydroxypropyl methacrylate.
7. A personal care composition according to claim 6, wherein said monomer units of each of said side chains is selected from the group consisting of acrylic acid, methacrylic acid, n-propyl methacrylate, iso-butyl methacrylate and mixtures thereof, wherein each side chain of said polymer has a Tg of from  $50^\circ\text{C}$  to  $200^\circ\text{C}$ .
8. An adhesive copolymer according to claim 1, wherein said backbone further comprises one or more side chains having a polysiloxane-containing macromonomer units, wherein said polysiloxane-containing macromonomer side chains have a weight average molecular weight from 1,000 to 50,000, and correspond to the chemical formula:  

$$X(Y)_nSi(R)_{3-m}(Z)_m$$
 wherein:  
 X is a vinyl group copolymerizable with said vinyl monomer units;  
 Y is a divalent linking group;  
 R is selected from the group consisting of hydrogen, hydroxyl, C1-C6 alkyl, C1-C6 alkoxy, C2-C6 alkylamino, phenyl, C1-C6 alky or alkoxy-substituted phenyl;  
 Z is a monovalent siloxane polymeric moiety having a number average molecular weight of at least 1000, is essentially unreactive under copolymerization conditions, and is pendant from said vinyl polymeric backbone after polymerization;  
 $n$  is 0 or 1; and  
 $m$  is an integer from 1 to 3.

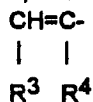
9. A An adhesive copolymer according to Claim 8 wherein said polysiloxane-containing macromonomer units are selected from the group consisting of:



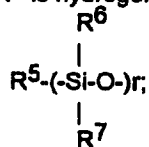
and



wherein  $s$  is 0, 1, 2, 3, 4, 5 or 6;  $m$  is 1, 2 or 3;  $p$  is 0;  $q$  is 2, 3, 4, 5 or 6;  $\text{R}^1$  is selected from the group consisting of hydrogen, hydroxyl, C1-C6 alkyl, C1-C6 alkoxy, C2-C6 alkylamino, phenyl, C1-C6 alkyl or alkoxy-substituted phenyl,  $\text{R}^2$  is selected from the group consisting of C1-C6 alkyl or C1-C6 alkyl substituted phenyl;  $n$  is 0, 1, 2, 3 or 4;  $\text{X}$  is

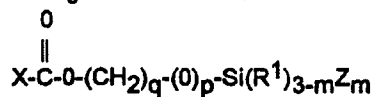


wherein  $\text{R}^3$  is hydrogen or  $-\text{COOH}$ ;  $\text{R}^4$  is hydrogen, methyl or  $-\text{CH}_2\text{COOH}$ ;  $\text{Z}$  is



$\text{R}^5$ ,  $\text{R}^6$ , and  $\text{R}^7$  independently are independently selected from the group consisting of hydrogen, hydroxyl, C1-C6 alkyl, C1-C6 alkoxy, C2-C6 alkylamino, phenyl, C1-C6 alkyl or alkoxy-substituted phenyl, and  $r$  is an integer of from 14 to 700.

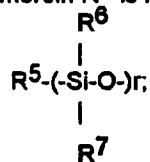
10. A An adhesive copolymer according to Claim 9 wherein said polysiloxane-containing macromonomer units correspond to the chemical formula:



wherein m is 1; p is 0; q is 3; R<sup>1</sup> is methyl; X is



wherein R<sup>3</sup> is hydrogen; R<sup>4</sup> is methyl; and Z is



R<sup>5</sup>, R<sup>6</sup>, and R<sup>7</sup> are independently selected from the group consisting of hydrogen, hydroxyl, C1-C6 alkyl, C1-C6 alkoxy, C2-C6 alkylamino, phenyl, C1-C6 alkyl or alkoxy-substituted phenyl, and r is an integer of from 14 to 700.



# INTERNATIONAL SEARCH REPORT

International Application No

PCT/IB 98/00702

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C09J151/00 A61K7/48

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C09J C08F A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 981 902 A (MITRA SMARAJIT ET AL) 1 January 1991 see column 5, line 61-66 ----	1-10
X	EP 0 491 169 A (LINTEC CORP) 24 June 1992 see page 5, line 4-15 see page 5, line 50-53 ----	1-10
P, X	EP 0 815 848 A (OREAL) 7 January 1998 see the whole document ----	1-7
X	EP 0 357 229 A (DU PONT) 7 March 1990 see page 4, line 13-49; claims 1,4 -----	1-4

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance  
 "E" earlier document but published on or after the international filing date  
 "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)  
 "O" document referring to an oral disclosure, use, exhibition or other means  
 "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention  
 "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone  
 "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.  
 "&" document member of the same patent family

Date of the actual completion of the international search

29 July 1998

Date of mailing of the international search report

05/08/1998

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
 NL - 2280 HV Rijswijk  
 Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
 Fax: (+31-70) 340-3016

Authorized officer

Meulemans, R

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/IB 98/00702

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4981902 A	01-01-1991	US RE34902 E US 4988506 A	11-04-1995 29-01-1991
EP 0491169 A	24-06-1992	JP 4216886 A DE 69107976 D DE 69107976 T US 5252395 A	06-08-1992 13-04-1995 13-07-1995 12-10-1993
EP 0815848 A	07-01-1998	FR 2750321 A JP 10059816 A	02-01-1998 03-03-1998
EP 0357229 A	07-03-1990	US 5006582 A CA 1332641 A DE 68912034 D DE 68912034 T JP 2167380 A JP 2730986 B US 5225470 A	09-04-1991 18-10-1994 17-02-1994 07-07-1994 27-06-1990 25-03-1998 06-07-1993

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
10 April 2003 (10.04.2003)

PCT

(10) International Publication Number  
**WO 03/028677 A1**

(51) International Patent Classification<sup>7</sup>: **A61K 7/06**,  
C08L 83/00

(21) International Application Number: PCT/EP02/10643

(22) International Filing Date:  
18 September 2002 (18.09.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
09/968,214 1 October 2001 (01.10.2001) US

(71) Applicant (for AE, AG, AU, BB, BZ, CA, GB, GD, GH, GM, IL, KE, LC, LK, LS, MN, MW, NZ, OM, SD, SG, SL, TT, TZ, UG, VC, ZA, ZM, ZW, SZ, CY, IE only): **UNILEVER PLC** [GB/GB]; Unilever House, Blackfriars, London EC4P 4BQ (GB).

(71) Applicant (for AL, AM, AT, AZ, BA, BG, BR, BY, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GE, HR, HU, ID, IS, JP, KG, KP, KR, KZ, LR, LT, LU, LV, MA, MD, MG, MK, MX, MZ, NO, PH, PL, PT, RO, RU, SE, SI, SK, TJ, TM, TN, TR, UA, UZ, VN, YU, BE, FR, GR, IT, MC, NL, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG only): **UNILEVER NV** [NL/NL]; Weena 455, NL-3013 AL Rotterdam (NL).

(71) Applicant (for IN only): **HINDUSTAN LEVER LIMITED** [IN/IN]; Hindustan Lever House, 165/166 Backbay Reclamation, Maharashtra, 400 020 Mumbai (IN).

(72) Inventors: **DHAMDHARE, Mrunalini**; Unilever Home & Personal Care USA, 3100 East Golf Road, Rolling Meadows, Chicago, IL 60008 (US). **EVANS, Trefor, Anthony**; Unilever Home & Personal Care USA, 3100 East Golf Road, Rolling Meadows, Chicago, IL 60008 (US). **SHAN, Yun**; 3810 Mykonos Lane, San Diego, CA 92130 (US). **MILCZAREK, Pawel, Włodzimierz**; Unilever Home & Personal Care USA, 3100 East Golf

Road, Rolling Meadows, Chicago, IL 60008 (US). **TAYLOR, Cheryl, Anne**; Unilever Research Port Sunlight, Quarry Road East, Bebington, Wirral, Merseyside CH63 3JW (GB). **BARBUZZI, Elena, Maria, Gabriella**; Unilever Research Port Sunlight, Quarry Road East, Bebington, Wirral, Merseyside CH63 3JW (GB). **WIRE, Stephen**; Unilever Research Port Sunlight, Quarry Road East, Bebington, Wirral, Merseyside CH63 3JW (GB). **BERGMANN, Wolfgang, Robert**; Unilever Home & Personal Care USA, 3100 East Golf Road, Rolling Meadows, Chicago, IL 60008 (US).

(74) Agents: **TANSLEY, Sally, Elizabeth** et al.; Unilever PLC, Patent Department, Colworth House, Sharnbrook, Bedford, Bedfordshire MK44 1LQ (GB).

(81) Designated States (national): AE, AG, AL, AM, AT (utility model), AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ (utility model), CZ, DE (utility model), DE, DK (utility model), DK, DM, DZ, EC, EE (utility model), EE, ES, FI (utility model), FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK (utility model), SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

**Published:**

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: **HAIR TREATMENT COMPOSITIONS WHICH PROVIDE HAIR BODY AND WHICH COMPRISE SILICONE PRESSURE SENSITIVE ADHESIVES**

(57) Abstract: An aqueous hair treatment composition comprising: a) at least one silicone pressure sensitive adhesive; and b) at least one material selected from the group consisting of a hair conditioning agent, a hair cleansing agent, and an agent for hair care suspension, is described.



WO 03/028677 A1

HAIR TREATMENT COMPOSITIONS WHICH PROVIDE HAIR BODY AND  
WHICH COMPRISE SILICONE PRESSURE SENSITIVE ADHESIVES

FIELD OF THE INVENTION

5

This invention relates to rinse-off hair treatment compositions and to their use in the treatment of hair.

BACKGROUND AND PRIOR ART

10

Shampoo compositions are generally formulated with highly effective cleansing surfactants, typically anionic surfactants, and do not in themselves provide much conditioning or styling benefit to the hair. In fact, basic shampoo formulations which have not been supplemented with specific conditioning or styling agents have a tendency to leave the hair in a cosmetically-unsatisfactory condition with regards to manageability and stylability. The hair tends to have a harsh, dull and dry feel, often referred to as "creak", is often difficult to comb, in either the wet or the dry state, typically has poor brushing properties, and tends to have poor set-retaining abilities.

20

This has resulted in the use of products containing specific conditioning and/or styling agents. Such agents are generally applied separately after shampooing and rinsing the hair, for example, in the form of conditioner formulations or styling mousses etc. Alternatively, conditioning and/or styling agents have been incorporated into the shampoo formulations. Although the latter approach provides the advantage of removing the need for a separate

25

30

- 2 -

conditioner or styling treatment, the conditioning and/or styling agents are not always compatible with the shampoo ingredients, especially the anionic surfactant. This can result in the cleansing action and/or cosmetic benefit being  
5 compromised.

One of the most common methods for imparting styling benefits to the hair has been the use of hair fixative agents, such as high molecular weight polymers. The problem  
10 with using such agents is that they have a tendency to negatively impact on conditioning attributes such as wet and dry stage clean feel and smoothness. In fact, they can result in a sticky feel to the hair.

15 Conventional styling polymers are typically water soluble. This means that when incorporated into a shampoo or conditioner which is rinsed off the hair, there is a tendency for the styling polymer to be washed away to a greater or lesser degree with the shampoo/conditioner.  
20 Hence, most styling products are leave-in products which are applied to the hair as post-shampoo/conditioner treatments.

The problem being addressed by the present invention is the provision of rinse-off hair treatment compositions which  
25 impart styling benefits, and in particular body benefits on the hair, but which do not compromise the cleansing action of the shampoo and which do not negatively impact on the conditioning attributes of the hair. The body benefits or attributes the present invention is looking particularly to  
30 provide include root lift, increased hair volume, bounce, control (i.e. ease of styling) and manageability, i.e.

- 3 -

maintenance of style without undue stiffness and negative sensory feel. Such body attributes are particularly attractive to people with fine or long, weighty hair.

5 One way in which this problem has been addressed in the past has been to include conditioning agents, for example silicones and cationic surfactants, in the compositions, to counter the negative effects of the styling agents. Although such conditioning agents do provide substantial  
10 improvements in for example the wet and dry combing properties of the hair and in the smoothness of the hair, they tend to have a negative effect on many of the attributes associated with hair body.

15 An alternative approach has been the use different forms of styling agents such as small particulate materials. Such an approach is described, for example, in our unpublished PCT International Patent Application No. PCT/GB00/04020. This document describes the use of small hard particles, and in  
20 particular colloidal silica, in hair treatment compositions to impart body and volume to the hair. Although providing significant styling benefits, the use of these materials can still lead to small levels of sensory negatives, such as for example a dry feel to the hair.

25

JP 10144622 (Toshiba Silicone) discloses cosmetic compositions containing particles consisting of colloidal silica cores surrounded by silicone shells which may be used on the skin or hair. Hairdressing lotions, hair creams and  
30 cleansing compositions such as a shampoo, rinse and

- 4 -

conditioner are disclosed as suitable cosmetic compositions in which the particles can be utilized.

We have now found that the inclusion of a certain level of  
5 silicone pressure sensitive adhesives (silicone PSA) in the hair treatment formulations provides substantial styling benefits, in particular with regards to imparting body attributes to the hair. Furthermore, the conditioning attributes of the hair are not adversely affected by the use  
10 of hair compositions containing these silicone PSA's and there is no necessity to incorporate additional conditioning agents or specialized surfactant systems. The compositions of the present invention are also stable.

15 The incorporation of silicone PSA's into the hair treatment compositions of this invention leads to substantive improvements in the body of the washed and optionally conditioned hair, especially if a subsequent styling regime is followed. The compositions impart body attributes, such  
20 as root lift, volume, bounce and manageability, in the absence (or substantial absence) of a styling polymer, which leads to compositions which have a styling benefit, but nevertheless do not suffer from the sensory negatives (e.g. stickiness and/or dry feel) which are associated with prior  
25 styling compositions which are based on, for example, a styling polymer.

#### SUMMARY OF THE INVENTION

30 Accordingly, this invention provides an aqueous hair treatment composition comprising:

- 5 -

- a) at least one silicone pressure sensitive adhesive
- b) a material selected from the group consisting of a suspending agent, a hair conditioning agent and a hair cleansing agent.

5

Preferably, the resulting hair care composition will increase static friction of dry hair by at least about 10%, and will increase in the dynamic friction of dry hair by no more than 100% or leave said dynamic friction unchanged or  
10 decrease said dynamic friction. This invention provides for the use of silicone PSA's as defined herein in a hair treatment composition to impart body without compromising conditioning.

#### 15 DETAILED DESCRIPTION OF THE INVENTION

Unless specified otherwise, all wt% values quoted hereinafter are percentages by weight based on total weight of the hair treatment composition.

20

Compositions of the invention may be prepared by known methods, or may be prepared by methods which are analogous to known methods.

25 By "insoluble" is meant that the material is not soluble in water (distilled or equivalent) at a concentration of 0.1%, at 25°C.

The invention provides an aqueous hair treatment composition  
30 comprising:



- 6 -

- a) at least one silicone pressure sensitive adhesive
- b) a material selected from the group consisting of a suspending agent, a hair conditioning agent and a hair cleansing agent.

5

Preferably, the resulting hair care composition will increase static friction of dry hair by at least 10%, or more preferably by at least about 15%, most preferably by about 20% and which increases the dynamic friction of dry hair by not more than 100%, or more preferably no more than by 60% or most preferably not more than by 40% Said dynamic friction of dry hair may also be unchanged or decrease.

More preferably, the invention provides an aqueous hair treatment composition comprising

- a) about 0.1% to about 10% of at least one silicone pressure sensitive adhesive;  
and
- b1) about 0.1% to about 10% of at least one suspending agent; or
- b2) about 0.05% to about 10% of at least one hair conditioning agent; or
- b3) about 5% to about 40% of at least one hair cleansing agent.

25

What follows now are descriptions of the materials and ingredients that may be employed in the compositions of the present invention.

- 7 -

## SILICONE PRESSURE SENSITIVE ADHESIVES

Pressure sensitive adhesives (PSA) are being used for a wide variety of adhesive applications. Organic PSAs have been  
5 finding increased utility principally for manufacture of adhesive tapes and labels. Other PSA uses include automotive, medical and coating industry applications. There are several chemical types of PSAs, including tackified natural rubbers, synthetic rubbers, polyvinyl  
10 ether types PSAs, acrylic, and silicone PSAs. The present invention relates to the use of Silicone PSAs in hair care applications.

PSAs require a delicate balance of viscous and elastic  
15 properties that results in desired balance of adhesion, cohesion, peel strength and elasticity. The performance of PSA is governed mainly by three properties: Tack, peel strength and shear strength. Properties such as shear strength, cohesion can be tested using standard tests that  
20 are found in the detail in literature (Ref: A. Zosel, J. *Adhesion*, 1994, 44, pp 1-6). Adhesion is the binding force between two different materials, whereas cohesion is the binding force between two similar materials. When two materials are brought into contact with each other, the  
25 surface molecules interact, giving rise to attractive forces that may be physical, chemical or electrostatic (corresponding to adsorption, covalent bonding or van der Waals forces, respectively). When the molecules are similar, as in the case of two 'glue molecules,' the  
30 cohesive force causes the glue to stick to itself. When the molecules are dissimilar, as in the case of a glue molecule

- 8 -

and a molecule of the substrate (the surface the glue is sticking to), the adhesive force holds the glue to the substrate. PSAs usually consist of chemical moieties that exhibit varying tackifying and elastomeric behaviors. By controlling the amount of the viscous and elastic materials, desired properties can be obtained. As used herein, the term PSA shall refer to an adhesive composition that satisfies the Dahlquist criterion, i.e.: 1 -sec creep compliance greater than  $1 \times 10^{-6}$  cm<sup>2</sup>/dyne (Ref: Handbook of Pressure Sensitive Adhesive Technology, p 172, D. Satas (ed.) Van Nostrand, N. Y. (1989)). Typically, a pressure sensitive adhesive is normally tacky at room temperature and adheres to a surface upon contact to the surface without the need for more than finger or hand pressure. Owing to the unique chemistry of PSAs, they exhibit some unique properties such as low glass transition temperature ( $T_g$ ), low surface energy, high flexibility, quick bonding.

This present invention relates to the use of silicone PSAs for hair care rinse-off applications. Silicone PSAs comprise two major components, a polymer or gum, and a tackifying resin. The polymer is typically a high molecular weight polydimethylsiloxane or polydimethyldiphenylsiloxane, that contains residual silanol functionality (SiOH) on the ends of the polymer chain, or a block copolymer comprising polydiorganosiloxane soft segments and urea terminated hard segments. The tackifying resin is generally a three dimensional silicate structure that is endcapped with trimethylsiloxy groups (OSiMe<sub>3</sub>) and also contains some residual silanol functionality. Manufacture of typical

- 9 -

silicone PSA is described in US patent 2736721 (Dexter). Other materials can be added for special purposes, including pigments, plasticizers, and fillers. Although, silicone PSAs have been cited in US patent 5337047, US patent 5060804  
5 and US patent 5451610.

A preferable silicone PSA can be a mixture of a hydroxy-terminated polydimethylsiloxane gum of  $T_g$  below  $-20^\circ\text{C}$  with a silicone resin which has a  $T_g$  or softening point above  $0^\circ\text{C}$ .  
10 The gum is lightly crosslinked with the resin. The resin comprises at least 30% units selected from  $\text{RSiO}_3/2$  units (T units) and  $\text{SiO}_4/2$  units (Q units), optionally together with  $\text{R}_3\text{SiO}_1/2$  units (M units) and/or  $\text{R}_2\text{SiO}_2/2$  units (D units), where R is a monovalent hydrocarbon radical, preferably  
15 methyl, and generally has an average of at least one R group per Si atom. The  $T_g$  of the blend of resin and gum is generally between  $-15$  and  $15^\circ\text{C}$  (T at tan delta maximum). The resin lowers the rubbery plateau modulus of the system. The resin is preferably a silanol-containing trimethylated  
20 silicate resin, that is a resin comprising Q and M units in which some trimethylsilyl groups are replaced by dimethylhydroxysilyl groups. The PSAs described above can be supplied as solutions or in emulsified form to be used in the hair care compositions of this invention.

25 A preferred silicone PSA emulsion can be prepared by mixing the silicone PSA in volatile silicone fluid. The silicone PSA together with a volatile silicone fluid having a boiling point below  $300^\circ\text{C}$  is emulsified together in water using one  
30 or more surfactants. The preferred surfactants are anionic

- 10 -

or nonionic surfactants, especially a blend of anionic and nonionic surfactants. The silicone fluid can be a linear polydiorganosiloxane such as hexamethyldisiloxane, octamethyltrisiloxane, decamethyltetrasiloxane, 5 dodecamethylpentasiloxane or a polydimethylsiloxane of viscosity 1cSt, or can be a cyclic siloxane such as decamethylcyclopentasiloxane or octamethylcyclotetrasiloxane or can be a mixture of one or more linear polydimethylsiloxanes with one or more cyclic siloxanes.

10

Silicone PSAs may be formed with a wide range of tack properties, peel adhesion properties and cohesion properties. In the hair care compositions of the present invention, it is also preferable that the silicone PSAs have 15 tack and adhesion properties in the following range:

	<b>Tack (g)</b>	<b>Adhesion (g/cm)</b>
Low tack (LT)	<70	800
Medium tack (MT)	70	600
High tack (HT)	500	400

20 In the hair care compositions of the present invention, it is also preferable that the silicone PSAs have tack properties between about 40 g to about 750 g, or more preferably 50 g to 600 g; adhesion properties between about 1600 g/cm to 200 g/cm, or more preferably 1000 g/cm to 300 25 g/cm.

Silicone PSA that may be used in the compositions of the invention may have a resin-to-polymer ratio that can range

- 11 -

from about 25 to 75 to about 75 to 25, more preferably from about 55 to 45 to 65 to 35.

5 In the hair care compositions of the present invention, the silicone PSAs can cause said compositions to maximally increase the dynamic friction of dry hair by 100% or 60%, or most preferably by 40%; and can cause the static friction of dry hair to increase by at least 10% or 15%, or most preferably by 20%.

10

This invention does not include the silicone acrylate type of PSAs, such as acrylate dimethicone copolymer cited in US patent 5166276 or acrylates/dimethicone methacrylate copolymer that have been previously used in hair care applications.

15

#### HAIR TREATMENT COMPOSITIONS

20 Compositions in accordance with the invention may be formulated as compositions for the treatment of hair and subsequent rinsing.

#### COMPOSITIONS MADE WITH A SUSPENDING AGENT

25 Compositions in accordance with this invention may also be formulated as suspensions for the treatment of hair and subsequent rinsing. These compositions will require silicone PSAs and a suspending agent.

- 12 -

Suspending agents:

In a preferred embodiment, the hair treatment composition further comprises from 0.01 to 10 wt% of a suspending agent  
5 for the silicone pressure sensitive adhesive. Suitable suspending agents are selected from polyacrylic acids, cross-linked polymers of acrylic acid, copolymers of acrylic acid with a hydrophobic monomer, copolymers of carboxylic acid-containing monomers and acrylic esters, cross-linked  
10 copolymers of acrylic acid and acrylate esters, heteropolysaccharide gums and crystalline long chain acyl derivatives. The long chain acyl derivative is desirably selected from ethylene glycol stearate, alkanolamides of fatty acids having from 16 to 22 carbon atoms and mixtures  
15 thereof. Ethylene glycol distearate and polyethylene glycol 3 distearate are preferred long chain acyl derivatives. Polyacrylic acid is available commercially as Carbopol 420, Carbopol 488 or Carbopol 493. Polymers of acrylic acid cross-linked with a polyfunctional agent may also be used,  
20 they are available commercially as Carbopol 910, Carbopol 934, Carbopol 940, Carbopol 941 and Carbopol 980. An example of a suitable copolymer of a carboxylic acid containing a monomer and acrylic acid esters is Carbopol 1342. All Carbopol (trade mark) materials are available  
25 from Goodrich.

Suitable cross-linked polymers of acrylic acid and acrylate esters are Pemulen TR1 or Pemulen TR2. A suitable heteropolysaccharide gum is xanthan gum, for example that  
30 available as Kelzan mu.

- 13 -

## COMPOSITIONS MADE WITH A CONDITIONING AGENT

Compositions in accordance with this invention may also be formulated as conditioners for the treatment of hair typically after shampooing and subsequent rinsing. These compositions will require silicone PSAs and a conditioning agent.

## Conditioning Agents

10

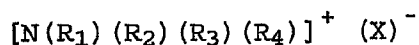
Such a conditioner will comprise at least one silicone pressure sensitive adhesive and one or more conditioning agents that are cosmetically acceptable and suitable for topical application to the hair.

15

Suitable conditioning agents are selected from cationic surfactants, used singly or in admixture.

Cationic surfactants useful in compositions of the invention contain amino or quaternary ammonium hydrophilic moieties which are positively charged when dissolved in the aqueous composition of the present invention.

Examples of suitable cationic surfactants are those corresponding to the formula:



in which  $R_1$ ,  $R_2$ ,  $R_3$ , and  $R_4$  are independently selected from (a) an aliphatic group of from 1 to 22 carbon atoms, or (b)



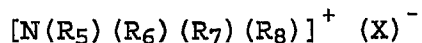
- 14 -

an aromatic, alkoxy, polyoxyalkylene, alkylamido, hydroxyalkyl, aryl or alkylaryl group having up to 22 carbon atoms; and X is a salt-forming anion such as those selected from halogen, (e.g. chloride, bromide), acetate, citrate, 5 lactate, glycolate, phosphate nitrate, sulphate, and alkylsulphate radicals.

The aliphatic groups can contain, in addition to carbon and hydrogen atoms, ether linkages, and other groups such as 10 amino groups. The longer chain aliphatic groups, e.g., those of about 12 carbons, or higher, can be saturated or unsaturated.

The most preferred cationic surfactants for conditioner 15 compositions of the present invention are monoalkyl quaternary ammonium compounds in which the alkyl chain length is C8 to C14.

Suitable examples of such materials correspond to the 20 formula:



in which R<sub>5</sub> is a hydrocarbyl chain having 8 to 14 carbon atoms 25 or a functionalized hydrocarbyl chain with 8 to 14 carbon atoms and containing ether, ester, amido or amino moieties present as substituents or as linkages in the radical chain, and R<sub>6</sub>, R<sub>7</sub> and R<sub>8</sub> are independently selected from (a) hydrocarbyl chains of from 1 to about 4 carbon atoms, or (b) 30 functionalized hydrocarbyl chains having from 1 to about 4

- 15 -

carbon atoms and containing one or more aromatic, ether, ester, amido or amino moieties present as substituents or as linkages in the radical chain, and X is a salt-forming anion such as those selected from halogen, (e.g. chloride, bromide), acetate, citrate, lactate, glycolate, phosphate nitrate, sulphate, and alkylsulphate radicals.

The functionalised hydrocarbyl chains (b) may suitably contain one or more hydrophilic moieties selected from alkoxy (preferably C<sub>1</sub>-C<sub>3</sub> alkoxy), polyoxyalkylene (preferably C<sub>1</sub>-C<sub>3</sub> polyoxyalkylene), alkylamido, hydroxyalkyl, alkylester, and combinations thereof.

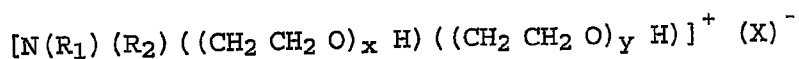
Preferably the hydrocarbyl chains R<sub>1</sub> have 12 to 14 carbon atoms, most preferably 12 carbon atoms. They may be derived from source oils which contain substantial amounts of fatty acids having the desired hydrocarbyl chain length. For example, the fatty acids from palm kernel oil or coconut oil can be used as a source of C<sub>8</sub> to C<sub>12</sub> hydrocarbyl chains.

Typical monoalkyl quaternary ammonium compounds of the above general formula for use in shampoo compositions of the invention include:

(i) lauryl trimethylammonium chloride (available commercially as Arquad C35 ex-Akzo); cocodimethyl benzyl ammonium chloride (available commercially as Arquad DMCB-80 ex-Akzo)

(ii) compounds of the formula:

- 16 -



wherein:

5     $x + y$  is an integer from 2 to 20;

$R_1$  is a hydrocarbyl chain having 8 to 14, preferably 12 to 14, most preferably 12 carbon atoms or a functionalised hydrocarbyl chain with 8 to 14, preferably 12 to 14, most  
10 preferably 12 carbon atoms and containing ether, ester, amido or amino moieties present as substituents or as linkages in the radical chain;

$R_2$  is a  $C_1$ - $C_3$  alkyl group or benzyl group, preferably methyl,  
15 and

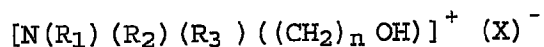
$X$  is a salt-forming anion such as those selected from halogen, (e.g. chloride, bromide), acetate, citrate, lactate, glycolate, phosphate nitrate, sulphate, methosulphate and  
20 alkylsulphate radicals.

Suitable examples are PEG- $n$  lauryl ammonium chlorides (where  $n$  is the PEG chain length), such as PEG-2 cocomonium chloride (available commercially as Ethoquad C12 ex-Akzo  
25 Nobel); PEG-2 cocobenzyl ammonium chloride (available commercially as Ethoquad CB/12 ex-Akzo Nobel); PEG-5 cocomonium methosulphate (available commercially as Rewoquat CPEM ex-Rewo); PEG-15 cocomonium chloride (available commercially as Ethoquad C/25 ex-Akzo)

30

- 17 -

(iii) compounds of the formula:



5 wherein:

n is an integer from 1 to 4, preferably 2;

10 R<sub>1</sub> is a hydrocarbyl chain having 8 to 14, preferably 12 to 14, most preferably 12 carbon atoms;

R<sub>2</sub> and R<sub>3</sub> are independently selected from C<sub>1</sub> - C<sub>3</sub> alkyl groups, and are preferably methyl, and

15 X<sup>-</sup> is a salt-forming anion such as those selected from halogen, (e.g. chloride, bromide), acetate, citrate, lactate, glycolate, phosphate nitrate, sulphate, and alkylsulphate radicals.

20 Suitable examples are lauryldimethylhydroxyethylammonium chloride (available commercially as Prapagen HY ex-Clariant)

Mixtures of any of the foregoing cationic surfactants compounds may also be suitable.

25

Examples of suitable cationic surfactants include:

quaternary ammonium chlorides, e.g. alkyltrimethylammonium chlorides wherein the alkyl group has from about 8 to 22  
30 carbon atoms, for example octyltrimethylammonium chloride,

- 18 -

dodecyltrimethylammonium chloride, hexadecyltrimethylammonium chloride, cetyltrimethylammonium chloride, octyldimethylbenzylammonium chloride, decyldimethylbenzylammonium chloride, stearyldi-  
5 methylbenzylammonium chloride, didodecyldimethylammonium chloride, dioctadecyldimethylammonium chloride, tallow trimethylammonium chloride, cocotrimethylammonium chloride, and the corresponding salts thereof, e.g., bromides, hydroxides. Cetylpyridinium chloride or salts thereof,  
10 e.g., chloride  
Quaternium -5  
Quaternium -31  
Quaternium -18  
and mixtures thereof.

15 In the conditioners of the invention, the level of cationic surfactant is preferably from 0.01 to 10, more preferably 0.05 to 5, most preferably 0.1 to 2 wt% of the total composition.

20 Optional Conditioning Materials

Fatty alcohol material

25 Conditioner compositions of the invention preferably additionally comprise a fatty alcohol material. The combined use of fatty alcohol materials and cationic surfactants in conditioning compositions is believed to be especially advantageous, because this leads to the formation of a  
30 lamellar phase, in which the cationic surfactant is dispersed.

- 19 -

By "fatty alcohol material" is meant a fatty alcohol, an alkoxyated fatty alcohol, or a mixture thereof.

Representative fatty alcohols comprise from 8 to 22 carbon  
5 atoms, more preferably 16 to 20. Examples of suitable fatty alcohols include cetyl alcohol, stearyl alcohol and mixtures thereof. The use of these materials is also advantageous in that they contribute to the overall conditioning properties of compositions of the invention.

10

Alkoxyated, (e.g. ethoxyated or propoxyated) fatty alcohols having from about 12 to about 18 carbon atoms in the alkyl chain can be used in place of, or in addition to, the fatty alcohols themselves. Suitable examples include  
15 ethylene glycol cetyl ether, polyoxyethylene (2) stearyl ether, polyoxyethylene (4) cetyl ether, and mixtures thereof.

The level of fatty alcohol material in conditioners of the  
20 invention is suitably from 0.01 to 15, preferably from 0.1 to 10, and more preferably from 0.1 to 5 wt%. The weight ratio of cationic surfactant to fatty alcohol is suitably from 10:1 to 1:10, preferably from 4:1 to 1:8, optimally from 1:1 to 1:7, for example 1:3.

25

#### Cationic Polymers

Conditioner compositions of the invention can also contain a cationic polymer. Suitable cationic polymers are described  
30 hereinbelow in relation to shampoo compositions.

- 20 -

# COMPOSITIONS MADE WITH A HAIR CLEANSING AGENT (SHAMPOO COMPOSITIONS)

A particularly preferred hair treatment composition in  
5 accordance with the invention is a shampoo composition that  
comprises of at least one silicone PSA and at least one  
cleansing agent.

Such a shampoo composition will comprise at least one  
10 silicone pressure sensitive adhesive and one or more  
cleansing surfactants which are cosmetically acceptable and  
suitable for topical application to the hair. Further  
surfactants may be present as an additional ingredient if  
sufficient for cleansing purposes is not provided as  
15 emulsifier for the silicone component. It is preferred that  
shampoo compositions of the invention comprise at least one  
further surfactant (in addition to that used as emulsifying  
agent for the silicone component) to provide a cleansing  
benefit.

20 Suitable cleansing agents, which may be used singularly or in  
combination, are selected from anionic, nonionic, amphoteric  
and zwitterionic surfactants, and mixtures thereof. The  
cleansing agent may be the same surfactant as the  
25 emulsifier, or may be different.

## CLEANSING AGENTS

Anionic cleansing surfactant

30

- 21 -

Shampoo compositions according to the invention will typically comprise one or more anionic cleansing surfactants which are cosmetically acceptable and suitable for topical application to the hair.

5

Examples of suitable anionic cleansing surfactants are the alkyl sulphates, alkyl ether sulphates, alkaryl sulphonates, alkanoyl isethionates, alkyl succinates, alkyl sulphosuccinates, N-alkyl sarcosinates, alkyl phosphates, 10 alkyl ether phosphates, alkyl ether carboxylates, and alpha-olefin sulphonates, especially their sodium, magnesium, ammonium and mono-, di- and triethanolamine salts. The alkyl and acyl groups generally contain from 8 to 18 carbon atoms and may be unsaturated. The alkyl ether sulphates, alkyl 15 ether phosphates and alkyl ether carboxylates may contain from 1 to 10 ethylene oxide or propylene oxide units per molecule.

Typical anionic cleansing surfactants for use in shampoo 20 compositions of the invention include sodium oleyl succinate, ammonium lauryl sulphosuccinate, ammonium lauryl sulphate, sodium dodecylbenzene sulphonate, triethanolamine dodecylbenzene sulphonate, sodium cocoyl isethionate, sodium lauryl isethionate and sodium N-lauryl sarcosinate. The most 25 preferred anionic surfactants are sodium lauryl sulphate, sodium lauryl ether sulphate(n)EO, (where n ranges from 1 to 3), ammonium lauryl sulphate and ammonium lauryl ether sulphate(n)EO, (where n ranges from 1 to 3).

30 Mixtures of any of the foregoing anionic cleansing surfactants may also be suitable.



- 22 -

The total amount of anionic cleansing surfactant in shampoo compositions of the invention is generally from 5 to 30, preferably from 6 to 20, more preferably from 8 to 16 wt%.

## 5 Amphoteric Surfactants

The shampoo composition can include other cleansing agents, to help impart aesthetic, physical or cleansing properties to the composition.

10

A preferred example is an amphoteric or zwitterionic surfactant, which can be included in an amount ranging from 0 to about 8, preferably from 1 to 4 wt%.

- 15 Examples of amphoteric and zwitterionic surfactants include alkyl amine oxides, alkyl betaines, alkyl amidopropyl betaines, alkyl sulphobetaines (sultaines), alkyl glycinate, alkyl carboxyglycinates, alkyl amphopropionates, alkylamphoglycinates, alkyl amidopropyl hydroxysultaines, acyl taurates and acyl glutamates, wherein the alkyl and acyl groups have from 8 to 19 carbon atoms. Typical amphoteric and zwitterionic surfactants for use in shampoos of the invention include lauryl amine oxide, cocodimethyl sulphopropyl betaine and preferably lauryl betaine, cocamidopropyl betaine and sodium cocamphopropionate.
- 20
- 25

## Nonionic Surfactants

- Another preferred example is a nonionic surfactant, which can be included in an amount ranging from 0 to 8, preferably from 2 to 5 wt%.
- 30

- 23 -

For example, representative nonionic surfactants that can be included in shampoo compositions of the invention include condensation products of aliphatic (C<sub>8</sub>-C<sub>18</sub>) primary or secondary linear or branched chain alcohols or phenols with alkylene oxides, usually ethylene oxide and generally having  
5 from 6 to 30 ethylene oxide groups.

Other representative nonionic surfactants include mono- or di-alkyl alkanolamides. Examples include coco mono- or di-  
10 ethanolamide and coco mono-isopropanolamide.

Further nonionic surfactants which can be included in shampoo compositions of the invention are the alkyl polyglycosides (APGs). Typically, the APG is one which comprises an alkyl  
15 group connected (optionally via a bridging group) to a block of one or more glycosyl groups. Preferred APGs are defined by the following formula:



20

wherein R is a branched or straight chain alkyl group which may be saturated or unsaturated and G is a saccharide group.

R may represent a mean alkyl chain length of from about C<sub>5</sub> to  
25 about C<sub>20</sub>. Preferably R represents a mean alkyl chain length of from about C<sub>8</sub> to about C<sub>12</sub>. Most preferably the value of R lies between about 9.5 and about 10.5. G may be selected from C<sub>5</sub> or C<sub>6</sub> monosaccharide residues, and is preferably a glucoside. G may be selected from the group comprising

- 24 -

glucose, xylose, lactose, fructose, mannose and derivatives thereof. Preferably G is glucose.

The degree of polymerization, n, may have a value of from  
5 about 1 to about 10 or more. Preferably, the value of n lies in the range of from about 1.1 to about 2. Most preferably the value of n lies in the range of from about 1.3 to about 1.5.

10 Suitable alkyl polyglycosides for use in the invention are commercially available and include for example those materials identified as: Oramix NS10 ex Seppic; Plantaren 1200 and Plantaren 2000 ex Henkel.

15 Other sugar-derived nonionic surfactants which can be included in shampoo compositions of the invention include the C<sub>10</sub>-C<sub>18</sub> N-alkyl (C<sub>1</sub>-C<sub>6</sub>) polyhydroxy fatty acid amides, such as the C<sub>12</sub>-C<sub>18</sub> N-methyl glucamides, as described for example in WO 92 06154 and US 5 194 639, and the N-alkoxy polyhydroxy  
20 fatty acid amides, such as C<sub>10</sub>-C<sub>18</sub> N-(3-methoxypropyl) glucamide.

#### OPTIONAL SHAMPOO INGREDIENTS

##### 25 Cationic Surfactants

The shampoo composition can also optionally include one or more cationic co-surfactants included in an amount ranging from 0.01 to 10, more preferably from 0.05 to 5, most  
30 preferably from 0.05 to 2 wt%. Useful cationic surfactants

- 25 -

are described hereinabove in relation to conditioner compositions.

The total amount of surfactant (including any co-surfactant,  
5 and/or any emulsifier) in shampoo compositions of the invention is generally from 5 to 50, preferably from 5 to

#### Cationic Polymer

10 A cationic polymer is a preferred ingredient in shampoo compositions of the invention, for enhancing conditioning performance of the shampoo.

The cationic polymer may be a homopolymer or be formed from two or more types of monomers. The molecular weight of the polymer will generally be between 5 000 and 10,000,000, typically at least 10 000 and preferably in the range 100 000 to about 2,000,000. The polymers will have cationic nitrogen containing groups such as quaternary ammonium or protonated amino groups, or a mixture thereof.

The cationic nitrogen-containing group will generally be present as a substituent on a fraction of the total monomer units of the cationic polymer. Thus when the polymer is not a homopolymer it can contain spacer non-cationic monomer units. Such polymers are described in the CTFA Cosmetic Ingredient Directory, 3rd edition. The ratio of the cationic to non-cationic monomer units is selected to give a polymer having a cationic charge density in the required range.

- 26 -

Suitable cationic conditioning polymers include, for example, copolymers of vinyl monomers having cationic amine or quaternary ammonium functionalities with water soluble spacer monomers such as (meth)acrylamide, alkyl and dialkyl (meth)acrylamides, alkyl (meth)acrylate, vinyl caprolactone and vinyl pyrrolidine. The alkyl and dialkyl substituted monomers preferably have C1-C7 alkyl groups, more preferably C1-3 alkyl groups. Other suitable spacers include vinyl esters, vinyl alcohol, maleic anhydride, propylene glycol and ethylene glycol.

The cationic amines can be primary, secondary or tertiary amines, depending upon the particular species and the pH of the composition. In general secondary and tertiary amines, especially tertiary, are preferred.

Amine substituted vinyl monomers and amines can be polymerized in the amine form and then converted to ammonium by quaternization.

The cationic conditioning polymers can comprise mixtures of monomer units derived from amine- and/or quaternary ammonium-substituted monomer and/or compatible spacer monomers.

Suitable cationic conditioning polymers include, for example:

- copolymers of 1-vinyl-2-pyrrolidine and 1-vinyl-3-methyl-imidazolium salt (e.g. chloride salt), referred to in the industry by the Cosmetic, Toiletry, and

- 27 -

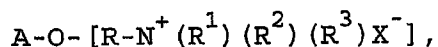
Fragrance Association, (CTFA) as Polyquaternium-16. This material is commercially available from BASF Wyandotte Corp. (Parsippany, NJ, USA) under the LUVIQUAT tradename (e.g. LUVIQUAT FC 370);

- copolymers of 1-vinyl-2-pyrrolidine and dimethylaminoethyl methacrylate, referred to in the industry (CTFA) as Polyquaternium-11. This material is available commercially from Gaf Corporation (Wayne, NJ, USA) under the GAFQUAT tradename (e.g., GAFQUAT 755N);
- cationic diallyl quaternary ammonium-containing polymers including, for example, dimethyldiallylammonium chloride homopolymer and copolymers of acrylamide and dimethyldiallylammonium chloride, referred to in the industry (CTFA) as Polyquaternium 6 and Polyquaternium 7, respectively;
- mineral acid salts of amino-alkyl esters of homo-and copolymers of unsaturated carboxylic acids having from 3 to 5 carbon atoms, (as described in U.S. Patent 4,009,256);
- cationic polyacrylamides (as described in WO95/22311).

Other cationic conditioning polymers that can be used include cationic polysaccharide polymers, such as cationic cellulose derivatives, cationic starch derivatives, and cationic guar gum derivatives. Suitably, such cationic polysaccharide polymers have a charge density in the range from 0.1 to 4 meq/g.

- 28 -

Cationic polysaccharide polymers suitable for use in compositions of the invention include those of the formula:



wherein: A is an anhydroglucose residual group, such as a starch or cellulose anhydroglucose residual. R is an alkylene, oxyalkylene, polyoxyalkylene, or hydroxyalkylene group, or combination thereof.  $R^1$ ,  $R^2$  and  $R^3$  independently represent alkyl, aryl, alkylaryl, arylalkyl, alkoxyalkyl, or alkoxyaryl groups, each group containing up to about 18 carbon atoms. The total number of carbon atoms for each cationic moiety (i.e., the sum of carbon atoms in  $R^1$ ,  $R^2$  and  $R^3$ ) is preferably about 20 or less, and  $X^-$  is an anionic counterion.

Cationic cellulose is available from Amerchol Corp. (Edison, NJ, USA) in their Polymer JR (trade mark) and LR (trade mark) series of polymers, as salts of hydroxyethyl cellulose reacted with trimethyl ammonium substituted epoxide, referred to in the industry (CTFA) as Polyquaternium 10. Another type of cationic cellulose includes the polymeric quaternary ammonium salts of hydroxyethyl cellulose reacted with lauryl dimethyl ammonium-substituted epoxide, referred to in the industry (CTFA) as Polyquaternium 24. These materials are available from Amerchol Corp. (Edison, NJ, USA) under the tradename Polymer LM-200.

Other suitable cationic polysaccharide polymers include quaternary nitrogen-containing cellulose ethers (e.g. as

- 29 -

described in U.S. Patent 3,962,418), and copolymers of etherified cellulose and starch (e.g. as described in U.S. Patent 3,958,581).

A particularly suitable type of cationic polysaccharide polymer that can be used is a cationic guar gum derivative, such as guar hydroxypropyltrimonium chloride (commercially available from Rhone-Poulenc in their JAGUAR trademark series).

Examples are JAGUAR C13S, which has a low degree of substitution of the cationic groups and high viscosity. JAGUAR C15, having a moderate degree of substitution and a low viscosity, JAGUAR C17 (high degree of substitution, high viscosity), JAGUAR C16, which is a hydroxypropylated cationic guar derivative containing a low level of substituent groups as well as cationic quaternary ammonium groups, and JAGUAR 162 which is a high transparency, medium viscosity guar having a low degree of substitution.

Preferably the cationic conditioning polymer is selected from cationic cellulose and cationic guar derivatives.

Particularly preferred cationic polymers are JAGUAR C13S, JAGUAR C15, JAGUAR C17 and JAGUAR C16 and JAGUAR C162.

The cationic conditioning polymer will generally be present in compositions of the invention at levels of from 0.01 to 5, preferably from 0.05 to 1, more preferably from 0.08 to 0.5  
5 wt%.



- 30 -

### Conditioning Agents

The compositions of this invention can also contain one or more conditioning agents selected from silicone conditioning  
5 agents and non-silicone oily conditioning agents.

When conditioning agent is present in the hair treatment compositions in droplet form, the droplets may be liquid, semi-solid or solid in nature, so long as they are  
10 substantially uniformly dispersed in the fully formulated product. Any droplets of oily conditioning agent are preferably present as either liquid or semi-solid droplets, more preferably as liquid droplets.

### 15 Silicone conditioning agents

The compositions of the invention can contain, emulsified droplets of a silicone conditioning agent, for enhancing conditioning performance. The silicone conditioning agent  
20 is insoluble in the aqueous matrix of the composition and so is present in an emulsified form, with the silicone present as dispersed droplets.

Suitable silicone conditioning agents include  
25 polydiorganosiloxanes, in particular polydimethylsiloxanes which have the CTFA designation dimethicone. Also suitable for use compositions of the invention (particularly shampoos and conditioners) are polydimethyl siloxanes having hydroxyl end groups, which have the CTFA designation dimethiconol.  
30 Also suitable for use in compositions of the invention are silicone gums having a slight degree of cross-linking, as

- 31 -

are described for example in WO 96/31188. These materials can impart body, volume and stylability to hair, as well as good wet and dry conditioning.

- 5 The viscosity of the emulsified silicone conditioning agent itself (not the emulsion or the final hair conditioning composition) is typically at least 10,000 cst. In general we have found that conditioning performance increases with increased viscosity. Accordingly, the viscosity of the
- 10 silicone conditioning agent itself is preferably at least 60,000 cst, most preferably at least 500,000 cst, ideally at least 1,000,000 cst. Preferably the viscosity does not exceed  $10^9$  cst for ease of formulation.
- 15 Emulsified silicone conditioning agents for use in the shampoo compositions of the invention will typically have an average silicone droplet size in the composition of less than 30, preferably less than 20, more preferably less than 10  $\mu\text{m}$ . We have found that reducing the droplet size
- 20 generally improves conditioning performance. Most preferably the average silicone droplet size of the emulsified silicone in the composition is less than 2  $\mu\text{m}$ , ideally it ranges from 0.01 to 1  $\mu\text{m}$ . Silicone emulsions having an average silicone droplet size of  $\leq 0.15 \mu\text{m}$  are
- 25 generally termed microemulsions.

Suitable silicone emulsions for use in the invention are also commercially available in a pre-emulsified form.

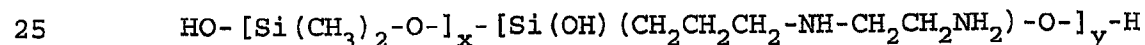
- 32 -

Examples of suitable pre-formed emulsions include emulsions DC2-1766, DC2-1784, and microemulsions DC2-1865 and DC2-1870, all available from Dow Corning. These are all emulsions/microemulsions of dimethiconol. Cross-linked silicone gums are also available in a pre-emulsified form, which is advantageous for ease of formulation. A preferred example is the material available from Dow Corning as DC 2-1787, which is an emulsion of cross-linked dimethiconol gum. A further preferred example is the material available from Dow Corning as DC 2-1391, which is a microemulsion of cross-linked dimethiconol gum.

A further preferred class of silicone conditioning agents for inclusion in shampoos and conditioners of the invention are amino functional silicones. By "amino functional silicone" is meant a silicone containing at least one primary, secondary or tertiary amine group, or a quaternary ammonium group.

Examples of suitable amino functional silicones include:

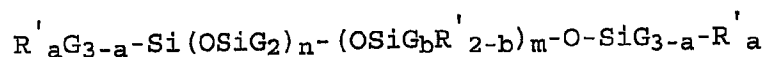
- (i) polysiloxanes having the CTFA designation "amodimethicone", and the general formula:



wherein x and y are numbers such that the molecular weight is between about 5,000 and 500,000.

- (ii) polysiloxanes having the formula:

- 33 -



in which:

- 5 G is selected from H, phenyl, OH or C<sub>1-8</sub> alkyl, e.g. methyl;  
 a is 0 or an integer from 1 to 3, preferably 0;  
 b is 0 or 1, preferably 1;  
 m and n are numbers such that (m + n) can range from 1 to  
 2000, preferably from 50 to 150;  
 10 m is a number from 1 to 2000, preferably from 1 to 10;  
 n is a number from 0 to 1999, preferably from 49 to 149, and

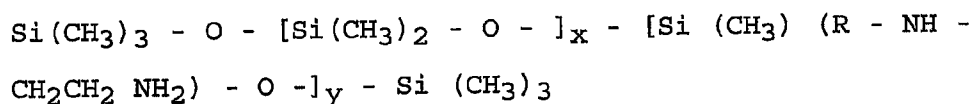
- R' is a monovalent radical of formula -C<sub>q</sub>H<sub>2q</sub>L in which q is a  
 number from 2 to 8 and L is an aminofunctional group selected  
 15 from the following:

- NR''-CH<sub>2</sub>-CH<sub>2</sub>-N(R'')<sub>2</sub>  
 -N(R'')<sub>2</sub>  
 -N<sup>+</sup>(R'')<sub>3</sub>A<sup>-</sup>  
 20 -N<sup>+</sup>H(R'')<sub>2</sub>A<sup>-</sup>  
 -N<sup>+</sup>H<sub>2</sub>(R'')A<sup>-</sup>  
 -N(R'')-CH<sub>2</sub>-CH<sub>2</sub>-N<sup>+</sup>H<sub>2</sub>(R'')A<sup>-</sup>

- in which R'' is selected from H, phenyl, benzyl, or a  
 25 saturated monovalent hydrocarbon radical, e.g. C<sub>1-20</sub> alkyl,  
 and A<sup>-</sup> is a halide ion, e.g. chloride or bromide.

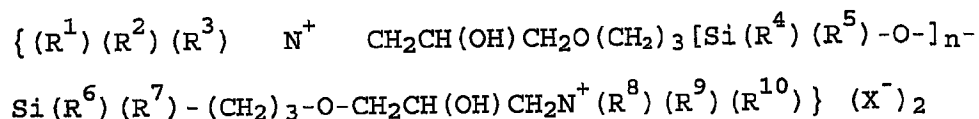
- 34 -

Suitable amino functional silicones corresponding to the above formula include those polysiloxanes termed "trimethylsilylamodimethicone" as depicted below, and which are sufficiently water insoluble so as to be useful in compositions of the invention:



wherein  $x + y$  is a number from about 50 to about 500, and wherein R is an alkylene group having from 2 to 5 carbon atoms. Preferably, the number  $x + y$  is in the range of from about 100 to about 300.

(iii) quaternary silicone polymers having the general formula:



wherein  $\text{R}^1$  and  $\text{R}^{10}$  may be the same or different and may be independently selected from H, saturated or unsaturated long or short chain alk(en)yl, branched chain alk(en)yl and C<sub>5</sub>-C<sub>8</sub> cyclic ring systems;

$\text{R}^2$  through  $\text{R}^9$  may be the same or different and may be independently selected from H, straight or branched chain lower alk(en)yl, and C<sub>5</sub>-C<sub>8</sub> cyclic ring systems;

- 35 -

n is a number within the range of about 60 to about 120, preferably about 80, and

X<sup>-</sup> is preferably acetate, but may instead be for example  
5 halide, organic carboxylate, organic sulphonate or the like.  
Suitable quaternary silicone polymers of this class are described in EP-A-0 530 974.

Amino functional silicones suitable for use in shampoos and  
10 conditioners of the invention will typically have a mole %  
amine functionality in the range of from about 0.1 to about  
8.0 mole %, preferably from about 0.1 to about 5.0 mole %, most preferably from about 0.1 to about 2.0 mole %. In  
general the amine concentration should not exceed about 8.0  
15 mole % since we have found that too high an amine  
concentration can be detrimental to total silicone  
deposition and therefore conditioning performance.

The viscosity of the amino functional silicone is not  
20 particularly critical and can suitably range from about 100  
to about 500,000 cSt.

Specific examples of amino functional silicones suitable for  
use in the invention are the aminosilicone oils DC2-8220,  
25 DC2-8166, DC2-8466, and DC2-8950-114 (all ex Dow Corning),  
and GE 1149-75, (ex General Electric Silicones).

Also suitable are emulsions of amino functional silicone  
oils with non ionic and/or cationic surfactant.

- 36 -

Suitably such pre-formed emulsions will have an average amino functional silicone droplet size in the shampoo composition of less than 30, preferably less than 20, more preferably less than 10  $\mu\text{m}$ . Again, we have found that  
5 reducing the droplet size generally improves conditioning performance. Most preferably the average amino functional silicone droplet size in the composition is less than 2  $\mu\text{m}$  ideally it ranges from 0.01 to 1  $\mu\text{m}$ .

10 Pre-formed emulsions of amino functional silicone are also available from suppliers of silicone oils such as Dow Corning and General Electric. Specific examples include DC929 Cationic Emulsion, DC939 Cationic Emulsion, and the non-ionic emulsions DC2-7224, DC2-8467, DC2-8177 and DC2-  
15 8154 (all ex Dow Corning).

An example of a quaternary silicone polymer useful in the present invention is the material K3474, ex Goldschmidt.

20 For shampoo compositions according to the invention intended for the treatment of "mixed" hair (i.e. greasy roots and dry ends), it is particularly preferred to use a combination of amino functional and non-amino functional silicone in compositions of the invention, especially when these are in  
25 the form of shampoo compositions. In such a case, the weight ratio of amino functional silicone to non-amino functional silicone will typically range from 1:2 to 1:20, preferably 1:3 to 1:20, more preferably 1:3 to 1:8. The total amount of silicone incorporated into compositions  
30 of the invention depends on the level of conditioning desired and the material used. A preferred amount is from

- 37 -

0.01 to 10 wt% although these limits are not absolute. The lower limit is determined by the minimum level to achieve conditioning and the upper limit by the maximum level to avoid making the hair and/or skin unacceptably greasy.

5

We have found that a total amount of silicone of from 0.3 to 5, preferably 0.5 to 3 wt% is a suitable level.

The viscosity of silicones and silicone emulsions can be  
10 measured by means of a glass capillary viscometer as set out further in Dow Corning Corporate Test Method CTM004, July 20 1970.

In compositions comprising silicone conditioning agent, it is  
15 preferred that a suspending agent for the silicone conditioning agent also be present. Suitable suspending agents are as described hereinabove.

Non-silicone oily conditioning components

20

Compositions according to the present invention may also comprise a dispersed, non-volatile, water-insoluble oily conditioning agent.

25 This component will be dispersed in the composition in the form of droplets, which form a separate, discontinuous phase from the aqueous, continuous phase of the composition. In other words, the oily conditioning agent will be present in the shampoo composition in the form of an oil-in-water  
30 emulsion.



- 38 -

Suitably, the  $D_{3,2}$  average droplet size of the oily conditioning component is at least 0.4, preferably at least 0.8, and more preferably at least 1  $\mu\text{m}$ . Additionally, the  $D_{3,2}$  average droplet size of the oily conditioning component is preferably no greater than 10, more preferably no greater than 8, more preferably no greater than 5, yet more preferably no greater than 4, and most preferably no greater than 3.5  $\mu\text{m}$ .

The oily conditioning agent may suitably be selected from oily or fatty materials, and mixtures thereof.

Oily or fatty materials are preferred conditioning agents in the shampoo compositions of the invention for adding shine to the hair and also enhancing dry combing and dry hair feel.

Preferred oily and fatty materials will generally have a viscosity of less than 5 Pa.s, more preferably less than 1 Pa.s, and most preferably less than 0.5 Pa.s, e.g. 0.1 Pa.s and under as measured at 25°C with a Brookfield Viscometer (e.g. Brookfield RV) using spindle 3 operating at 100 rpm.

Oily and fatty materials with higher viscosities may be used. For example, materials with viscosities as high as 65 Pa.s may be used. The viscosity of such materials (i.e. materials with viscosities of 5 Pa.s and greater) can be measured by means of a glass capillary viscometer as set out further in Dow Corning Corporate Test Method CTM004, July 20 1970.

30

- 39 -

Suitable oily or fatty materials are selected from hydrocarbon oils, fatty esters and mixtures thereof.

Hydrocarbon oils include cyclic hydrocarbons, straight chain  
5 aliphatic hydrocarbons (saturated or unsaturated), and  
branched chain aliphatic hydrocarbons (saturated or  
unsaturated). Straight chain hydrocarbon oils will  
preferably contain from about 12 to about 30 carbon atoms.  
Branched chain hydrocarbon oils can and typically may  
10 contain higher numbers of carbon atoms. Also suitable are  
polymeric hydrocarbons of alkenyl monomers, such as C<sub>2</sub>-C<sub>6</sub>  
alkenyl monomers. These polymers can be straight or  
branched chain polymers. The straight chain polymers will  
typically be relatively short in length, having a total  
15 number of carbon atoms as described above for straight chain  
hydrocarbons in general. The branched chain polymers can  
have substantially higher chain length. The number average  
molecular weight of such materials can vary widely, but will  
typically be up to about 2000, preferably from about 200 to  
20 about 1000, more preferably from about 300 to about 600.

Specific examples of suitable hydrocarbon oils include  
paraffin oil, mineral oil, saturated and unsaturated  
dodecane, saturated and unsaturated tridecane, saturated and  
25 unsaturated tetradecane, saturated and unsaturated  
pentadecane, saturated and unsaturated hexadecane, and  
mixtures thereof. Branched-chain isomers of these  
compounds, as well as of higher chain length hydrocarbons,  
can also be used. Exemplary branched-chain isomers are  
30 highly branched saturated or unsaturated alkanes, such as  
the permethyl-substituted isomers, e.g., the permethyl-

- 40 -

substituted isomers of hexadecane and eicosane, such as 2, 2, 4, 4, 6, 6, 8, 8-dimethyl-10-methylundecane and 2, 2, 4, 4, 6, 6-dimethyl-8-methylnonane, sold by Permethyl Corporation. A further example of a hydrocarbon polymer is  
5 polybutene, such as the copolymer of isobutylene and butene. A commercially available material of this type is L-14 polybutene from Amoco Chemical Co. (Chicago, Ill., U.S.A.).

Particularly preferred hydrocarbon oils are the various  
10 grades of mineral oils. Mineral oils are clear oily liquids obtained from petroleum oil, from which waxes have been removed, and the more volatile fractions removed by distillation. The fraction distilling between 250°C to 300°C is termed mineral oil, and it consists of a mixture of  
15 hydrocarbons ranging from  $C_{16}H_{34}$  to  $C_{21}H_{44}$ . Suitable commercially available materials of this type include Sirius M85 and Sirius M125, all available from Silkolene.

Suitable fatty esters are characterized by having at least  
20 10 carbon atoms, and include esters with hydrocarbyl chains derived from fatty acids or alcohols, e.g., monocarboxylic acid esters, polyhydric alcohol esters, and di- and tricarboxylic acid esters. The hydrocarbyl radicals of the fatty esters hereof can also include or have covalently  
25 bonded thereto other compatible functionalities, such as amides and alkoxy moieties, such as ethoxy or ether linkages.

Monocarboxylic acid esters include esters of alcohols and/or  
30 acids of the formula  $R'COOR$  in which  $R'$  and  $R$  independently

- 41 -

denote alkyl or alkenyl radicals and the sum of carbon atoms in R' and R is at least 10, preferably at least 20.

Specific examples include, for example, alkyl and alkenyl  
5 esters of fatty acids having aliphatic chains with from  
about 10 to about 22 carbon atoms, and alkyl and/or alkenyl  
fatty alcohol carboxylic acid esters having an alkyl and/or  
alkenyl alcohol-derived aliphatic chain with about 10 to  
about 22 carbon atoms, benzoate esters of fatty alcohols  
10 having from about 12 to 20 carbon atoms.

The monocarboxylic acid ester need not necessarily contain  
at least one chain with at least 10 carbon atoms, so long as  
the total number of aliphatic chain carbon atoms is at least  
15 10. Examples include isopropyl isostearate, hexyl laurate,  
isohexyl laurate, isohexyl palmitate, isopropyl palmitate,  
decyl oleate, isodecyl oleate, hexadecyl stearate, decyl  
stearate, isopropyl isostearate, dihexyldecyl adipate,  
lauryl lactate, myristyl lactate, cetyl lactate, oleyl  
20 stearate, oleyl oleate, oleyl myristate, lauryl acetate,  
cetyl propionate, and oleyl adipate.

Di- and trialkyl and alkenyl esters of carboxylic acids can  
also be used. These include, for example, esters of C<sub>4</sub>-C<sub>8</sub>  
25 dicarboxylic acids such as C<sub>1</sub>-C<sub>22</sub> esters (preferably C<sub>1</sub>-C<sub>6</sub>)  
of succinic acid, glutaric acid, adipic acid, hexanoic acid,  
heptanoic acid, and octanoic acid. Examples include  
diisopropyl adipate, diisohexyl adipate, and diisopropyl  
sebacate. Other specific examples include isocetyl stearyl  
30 stearate, and tristearyl citrate.

- 42 -

Polyhydric alcohol esters include alkylene glycol esters, for example ethylene glycol mono and di-fatty acid esters, diethylene glycol mono- and di-fatty acid esters, polyethylene glycol mono- and di-fatty acid esters, 5 propylene glycol mono- and di-fatty acid esters, polypropylene glycol monooleate, polypropylene glycol monostearate, ethoxylated propylene glycol monostearate, polyglycerol poly-fatty acid esters, ethoxylated glyceryl monostearate, 1,3-butylene glycol monostearate, 1,3-butylene 10 glycol distearate, polyoxyethylene polyol fatty acid ester, sorbitan fatty acid esters, polyoxyethylene sorbitan fatty acid esters and mono-, di- and triglycerides.

Particularly preferred fatty esters are mono-, di- and 15 triglycerides, more specifically the mono-, di-, and tri-esters of glycerol and long chain carboxylic acids such as C<sub>1</sub>-C<sub>22</sub> carboxylic acids. A variety of these types of materials can be obtained from vegetable and animal fats and oils, such as coconut oil, castor oil, safflower oil, 20 sunflower oil, cottonseed oil, corn oil, olive oil, cod liver oil, almond oil, avocado oil, palm oil, sesame oil, peanut oil, lanolin and soybean oil. Synthetic oils include triolein and tristearin glyceryl dilaurate.

25 Specific examples of preferred materials include cocoa butter, palm stearin, sunflower oil, soyabean oil and coconut oil.

The oily or fatty material is suitably present at a level of 30 from 0.05 to 10, preferably from 0.2 to 5, more preferably from about 0.5 to 3 wt%.

- 43 -

The compositions of this invention preferably contain no more than 3 wt% of a styling polymer, more preferably less than 1% of a styling polymer, preferably contain less than 0.1% by weight a styling polymer, and optimally are free of styling polymer.

In hair treatment compositions containing a conditioning agent, it is preferred that a cationic polymer also be present.

10

#### Adjuvants

The compositions of the present invention may also contain adjuvants suitable for hair care. Generally such ingredients are included individually at a level of up to 2, preferably up to 1 wt% of the total composition.

Among suitable hair care adjuvants, are:

- 20 (i) natural hair root nutrients, such as amino acids and sugars. Examples of suitable amino acids include arginine, cysteine, glutamine, glutamic acid, isoleucine, leucine, methionine, serine and valine, and/or precursors and derivatives thereof. The amino acids may be added singly, in mixtures, or in the form of peptides, e.g. di- and tripeptides. The amino acids may also be added in the form of a protein hydrolysate, such as a keratin or collagen hydrolysate. Suitable sugars are glucose, dextrose and fructose. These may be added singly or in the form of, e.g.
- 25 fruit extracts. A particularly preferred combination of natural hair root nutrients for inclusion in compositions of
- 30

- 44 -

the invention is isoleucine and glucose. A particularly preferred amino acid nutrient is arginine.

(ii) hair fibre benefit agents. Examples are:

5

- ceramides, for moisturizing the fibre and maintaining cuticle integrity. Ceramides are available by extraction from natural sources, or as synthetic ceramides and pseudoceramides. A preferred ceramide is Ceramide II, ex
- 10 Quest. Mixtures of ceramides may also be suitable, such as Ceramides LS, ex Laboratoires Serobiologiques.

The invention will now be further illustrated by the following, non-limiting Examples.

Table 1

Ingredient	Example 1 Weight %	Example 2 Weight %	Example 3 Weight %	Example 4 Weight %	Example 5 Weight %	Example 6 Weight %
Stearamidopropyl dimethylamine,	0.750	0.750	0.750	0.750	0.750	0.750
PEG-2 oleammonium chloride & propylene glycol	2.000	2.000	2.000	2.000	2.000	2.000
Behentrimonium Methosulfate and cetearyl alcohol	0.25	1.000	1.000	1.000	1.000	1.000
Cetyl alcohol	3.000	3.000	3.000	3.000	3.000	3.000
Stearyl alcohol	2.000	2.000	2.000	2.000	2.000	2.000
Disodium EDTA	0.100	0.100	0.100	0.100	0.100	0.100
Dimethiconol	0.000	0.000	0.000	0.000	0.8	0.000
Silicone Fluid 245	0.000	0.000	0.000	0.000	2.000	0.000
Fragrance	0.600	0.600	0.600	0.600	0.600	0.600
Low Tack Silicone PSA emulsion <sup>1</sup>	0.000	0.2	0.4	0.4	0.000	0.000
Colloidal silica	0.5	0.000	0.000	0.000	0.000	0.000
Water, fragrance, preservatives	q.s.	q.s.	q.s.	q.s.	q.s.	q.s.
Total	100.00	100.00	100.00	100.00	100.00	100.00

5                   <sup>1</sup> Low Tack Silicone PSA emulsion is available from Dow Corning Corp. (DC 5-7300)

which is a 40% emulsion of silicone PSA that contains 65% silicone resin and 35% silicone polymer.



- 46 -

Table 2:

	Example 7	Example 8	Example 9	Example 10	Example 11
Ingredient	Weight %	Weight %	Weight %	Weight %	Weight %
Water, soft	45.000	45.000	45.000	45.000	45.000
Hydroxyethylcellulose	0.200	0.000	0.000	0.000	0.200
Cetrimonium Chloride	2.800	2.500	2.500	2.500	2.800
Quaternium-18 and propylene glycol	0.500	0.400	0.400	0.400	0.500
Cetyl/Stearyl alcohol	3.000	3.000	3.000	3.000	3.000
Disodium EDTA, 100% active	0.100	0.100	0.100	0.100	0.100
Dimethiconol	0.8	0.6	0.6	0.6	0.8
Silicone fluid 245	0.000	0.000	0.000	0.000	0.000
Fragrance	0.400	0.400	0.600	0.600	0.600
Low Tack Silicone PSA emulsion <sup>1</sup>	0.000	0.000	0.000	0.500	0.000
Water, Fragrance, Preservative	q.s.	q.s.	q.s.	q.s.	q.s.
Total	100.000	100.000	100.000	100.000	100.000

5

Measurement of Static and Dynamic friction:

Friction measurements are performed using a modified version of a previously described methodology based on Dynamic Mechanical Analysis (DMA) (Ref: US Patent No. 5,968,286 which is hereby incorporated by reference). Testing involves the application of different force profiles to a bundle of hair fibers. One manner for carrying out testing involves using a single cantilever geometry wherein only one side of a hair bundle is secured. The extent to which the bundle deflects under force will possess a dependance on the

10

15

- 47 -

interfiber friction. As such, relative differences in the frictional properties of hair can be measured by comparing the results from treated and untreated hair bundles. A diagram of the experimental set up is shown below in Figure 1.

Two-gram hair tresses are prepared using natural brown hair purchased from Imhair Ltd. (Italy). Before testing, all tresses are cleaned thoroughly using standard surfactant solutions. Each tress is cut to the length of 6 inches. Testing is performed with the hair encased in a thin-walled latex tube with an inside diameter of 3 mm, and outside diameter 3.4 mm. A close up of the hair and the tube is shown in Figure 2.

For statistical purposes, 4 tube samples are tested for each formulation. Testing is first performed on an untreated hair array. After testing, the hair is removed from the latex tube and treated with the test formula. The formula is applied in the proportion 0.2 ml to 2 g of hair for a shampoo, and 0.3 ml to 2 g of hair for a conditioner product. Each hair array is treated for 1 minute and then rinsed for 30 seconds in warm water (40°C), at a flow rate of 2 l/min. After treatment the arrays are air dried for 24 hours at 30% RH, and a temperature of 20°C. The samples are then placed back in the latex tube and equilibrated for the next 24 hours under the same conditions. The treated hair arrays are then tested again to allow for differences in deflection to be observed as a result of surface modification imparted by the test material.

- 48 -

A Perkin Elmer DMA 7e housed within an environmentally controlled chamber is used for all our measurements. The tube sample is mounted in the single cantilever DMA fixture in such a way that the length of the latex tube protruding from the clamp is 20 mm (see Fig.1). The instrument probe imposes a bending force on the top of the tube at a distance of 7.5 mm from the clamp.

By imposing different force profiles, it is possible to measure different frictional properties of the hair. For example, a measure of the static friction can be obtained by performing a test in which the bending force is gradually increased. Meanwhile, the dynamic friction is measured by imposing an oscillating sinusoidal force. In each case, the instrument measures the resulting deflection or strain that results in the specimen. More detailed information regarding these two modes of operation are given below.

#### Change in static friction

The coefficient of static friction is calculated from a test in which an increasing bending force deflects the tube sample. Initially, the process is elastic and consequently a linear relationship exists between the stress (force/unit area) and the deflection. Under these conditions the array behaves like a solid rod, since the interfiber friction and the external pressure of the tube holds the fibers together and prevents movement of the individual fibers. However, at a certain critical force, adjacent fibers will start to slide over one another. As the result of this interfiber slip, the total resistance of the sample towards the bending

- 49 -

force decreases. From this point on, the deflection increases faster than the bending stress. That is, the linear relationship between the stress and strain is lost. The critical deflection  $d_c$  at which the interfiber slip  
5 appears is measured by the instrument and can be used to calculate an average coefficient of internal static friction in the tube sample. The change in static friction is calculated by comparing the critical deflection of the same hair array before and after treatment with the test sample.

10

#### Change in dynamic friction

The dynamic friction test is somewhat more complex. The use of an oscillating force allows for the deconvolution of a  
15 material's elastic (storage) and viscous (lost) components. These quantities identify the ability of the material to recover from deformation (elasticity) or to dissipate a portion of the mechanical energy (damping). Friction is a property that is associated with the dissipation of the  
20 mechanical energy and therefore can be probed using the loss component that is obtained from a dynamic mechanical test.

Dynamic friction testing is performed by introducing a gradually increasing dynamic force to the sample at a  
25 constant frequency. Furthermore, this dynamic force is superimposed over a gradually increasing static force. This behavior is shown schematically in Figure. 3.

Calculation of the coefficient of dynamic friction is more  
30 complex and requires a detailed analysis involving the movement of the fiber bundle as a result of the two

- 50 -

superimposed bending forces. As the magnitude of both the static and dynamic force is raised, so the magnitude of the deflection also increases. That is, the amplitude of dynamic bending also increases. Furthermore, the magnitude  
5 of the bending amplitude is influenced by the surface frictional properties of the hair fibers. The measurement of the amplitude before and after the treatment allows for assessment of a relative change in dynamic friction  $\Delta f_d$ .

The relative coefficient of dynamic friction is calculated  
10 by:

$$\Delta f_d / f_d = (A_U - A_T) / A_U$$

where  $A_U$  is the maximum amplitude of bending before treatment, and  $A_T$  is the maximum amplitude for the same hair array after the treatment.

15 If the same hair array were treated with a conditioning formula that reduces the surface friction, then the same bending force would be able to generate longer interfiber slip and the higher amplitude of bending (Fig. 4). The results of frictional tests are valid only for the  
20 treatments, which do not change the bulk properties of hair fibers, but only their surface friction.

The experimental data below demonstrates the beneficial properties of compositions of the invention.

- 51 -

Table 3 includes the static and dynamic friction properties as measured by the above mentioned DMA technique for the formulation examples as listed in tables 1 and 2.

5

Table 3

Conditioner Description	Static Friction (%)	Dynamic Friction (%)
Example 1	210	280
Example 2	17	3
Example 3	31	5
Example 4	45	26
Example 5	30	2
Example 6	-21	-29
Example 7	-10	-31
Example 8	25	-11
Example 9	-17.67	-22.67
Example 10	24	25
Example 11	-16	-29

#### Shampoo compositions:

The invention will now be further illustrated by the following, non-limiting example 12 of a shampoo formulation.

10

Table 4

Ingredient	Example 12 Weight %	Example 13 Weight %
Emulsion stabilizer	0.400	0.400
Ammonium Lauryl Sulphate	7.605	7.605
Ammonium Laureth Sulphate	5.941	5.941
Cocamide MEA	1.300	1.300
PEG-6 Cocamide	0.650	0.650
Propylene Glycol	0.500	0.500
Guar Hydroxypropyltrimonium chloride	0.100	0.100
Dimethiconol	1.000	1.000
Low Tack Silicone PSA <sup>1</sup>	0.000	0.750
Chelating agent	0.080	0.080
Water, Fragrance, and Preservatives	q.s.	q.s.

- 52 -

Table 5 includes the static and dynamic friction properties as measured by the above mentioned DMA technique for the formulation examples as listed in tables 4.

5

Table 5

Shampoo Description	Static Friction (%)	Dynamic Friction (%)
Example 12	-7	-11
Example 13	18	3

Suspension Composition:

- 10 The invention will now be further illustrated by the following, non-limiting examples of a suspension.

Example 13	
Description	Wt. %
Silicone PSA emulsion (40% active)	2.00
Carbopol 980, 100% active	1.00
DMDM Hydantion	0.1
Kathon CG, 39% active	0.04
Soft water, 100% active	96.86
<b>Total</b>	<b>100.00</b>

- 53 -

**CLAIMS**

1. An aqueous hair treatment composition comprising:
  - a) at least one silicone pressure sensitive adhesive;
  - 5 and
  - b) at least one material selected from the group consisting of:
    - i) a hair conditioning agent,
    - ii) a hair cleansing agent, and
    - 10 iii) an agent for suspending said silicone pressure sensitive adhesive in a manner which enables said silicone pressure sensitive adhesive to be deposited on said hair.
- 15 2. An aqueous hair treatment composition according to claim 1 wherein said composition increases static friction of dry hair by at least about 10%, and wherein said composition increases dynamic friction of dry hair by no more than about 100% or decreases or leaves unchanged  
20 said dynamic friction.
3. An aqueous hair treatment composition according to claim 2 wherein said composition increases dynamic friction of dry hair by no more than about 60%.
- 25 4. An aqueous hair treatment composition according to claim 2 wherein said composition increases dynamic friction of dry hair by no more than about 40%.



- 54 -

5. An aqueous hair treatment composition according to claim 2 wherein said composition increases static friction of dry hair by at least about 15%.
- 5 6. An aqueous hair treatment composition according to claim 2 wherein said composition increases static friction of dry hair by at least about 20%.
- 10 7. A composition in accordance with claim 1, wherein said silicone pressure sensitive adhesive is the product of mixing 30 to 60 parts by weight of a silanol-terminated polydiorganosiloxane of  $T_g$  below  $-20^{\circ}\text{C}$  and viscosity 0.1-30000 Pa.s at  $25^{\circ}\text{C}$  lightly crosslinked with 40 to 70 parts by weight of a silanol-containing silicone resin
- 15 of  $T_g$  above  $0^{\circ}\text{C}$  comprising monovalent trihydrocarbonsiloxy (M) groups of the formula  $\text{R}''_3\text{SiO}_{1/2}$  and tetrafunctional (Q) groups  $\text{SiO}_{4/2}$  wherein  $\text{R}''$  denotes a monovalent hydrocarbon group having 1 to 6 carbon atoms, the number ratio of M groups to Q groups being in
- 20 the range 0.5:1 to 1.2:1.
8. A composition in accordance to claim 1, wherein said pressure sensitive adhesive is dispersed as an emulsion comprising a disperse silicone phase emulsified in a
- 25 continuous water phase in the presence of a surfactant, wherein the disperse silicone phase comprises 40 to 80 % by weight of a silicone pressure sensitive adhesive, which is the lightly crosslinked product of mixing a silanol-terminated polydiorganosiloxane of  $T_g$  below -
- 30  $20^{\circ}\text{C}$  with a silanol-containing silicone resin of  $T_g$

- 55 -

above 0°C, dispersed in 60 to 20 % by weight of a volatile silicone fluid having a boiling point below 300°C, the emulsion being substantially free of any non-silicon-containing volatile organic material.

5

9. An aqueous hair treatment composition according to claim 1 comprising:

- 10 a) about 0.01% to about 10% of at least one silicone pressure sensitive adhesive; and
- b1) about 0.01% to about 10% of at least one suspending agent; or
- b2) about 0.05% to about 10% of at least one hair conditioning agent; or
- 15 b3) about 5% to about 40% of at least one hair cleansing agent.

10. An aqueous hair treatment composition according to claim 8 comprising:

20

- a) about 0.05% to about 5% of at least one silicone pressure sensitive adhesive; and
- b1) about 0.1% to about 5% of at least one suspending agent; or
- 25 b2) about 0.1% to about 5% of at least one hair conditioning agent; or
- b3) about 10% to about 20% of at least one hair cleansing agent.

30 11. An aqueous hair treatment composition according to claim 1 which is a leave-in composition.

- 56 -

12. An aqueous hair treatment composition according to claim 1 which is a rinse-out composition.
13. A composition according to claim 1 which is a hair  
5 conditioner and which comprises a conditioning agent selected from the group consisting of :  
octyltrimethylammonium chloride,  
dodecyltrimethylammonium chloride,  
hexadecyltrimethylammonium chloride,  
10 cetyltrimethylammonium chloride,  
octyldimethylbenzylammonium chloride,  
decyldimethylbenzylammonium chloride, stearyldi-  
methylbenzylammonium chloride, didodecyldimethylammonium  
chloride, dioctadecyldimethylammonium chloride, tallow  
15 trimethylammonium chloride, cocotrimethylammonium  
chloride, Cetylpyridinium chloride, Quaternium -5  
Quaternium -31 Quaternium -18;  
and mixtures thereof.
- 20 14. A composition in accordance with claim 1 which comprises  
a suspending agent selected from the group consisting of  
polyacrylic acids, cross-linked polymers of acrylic  
acid, copolymers of acrylic acid with a hydrophobic  
monomer, copolymers of carboxylic acid-containing  
25 monomers and acrylic esters, cross-linked copolymers of  
acrylic acid and acrylate esters, heteropolysaccharide  
gum; ethylene glycol stearate, alkanolamides of fatty  
acids ; ethylene glycol distearate; polyethylene glycol  
3 distearate; Carbopol 420, Carbopol 488; Carbopol 493;  
30 Carbopol 910, Carbopol 934, Carbopol 940, Carbopol 941;  
Carbopol 980; Carbopol 1342; cross-linked polymers of

- 57 -

acrylic acid and acrylate ester , xanthan gum, and mixtures thereof

15. A composition in accordance with claim 1 which is a  
5 shampoo and which comprises a hair cleansing agent selected from the group consisting of an anionic surfactant, a non-ionic surfactant, an amphoteric surfactant, and mixtures thereof.
- 10 16. A composition in accordance with claim 14 wherein said hair cleansing agent is selected from the group consisting of sodium dodecylbenzene sulphonate, sodium, lauryl sulphate, sodium lauryl ether sulphate nEO, where  
15 n is from 1 to 20; octylphenol ether sulphate nEO where n is from 1 to 20, sodium dioctylsulphosuccinate; nonylphenol ethoxylate nEO, where n is from 1 to 50, alcohol ethoxylates; lauryl alcohol nEO, where n is from 1 to 50, polyoxyethylene monostearate where the number  
20 of oxyethylene units is from 1 to 30.
17. A composition in accordance with claim 1, which  
comprises a conditioning agent selected from the group  
consisting of a volatile silicone, a nonvolatile  
silicone, and mixtures thereof .
- 25 18. A method for providing hair with body which comprises contacting said hair with a composition in accordance with claim 1.

Fig.1.

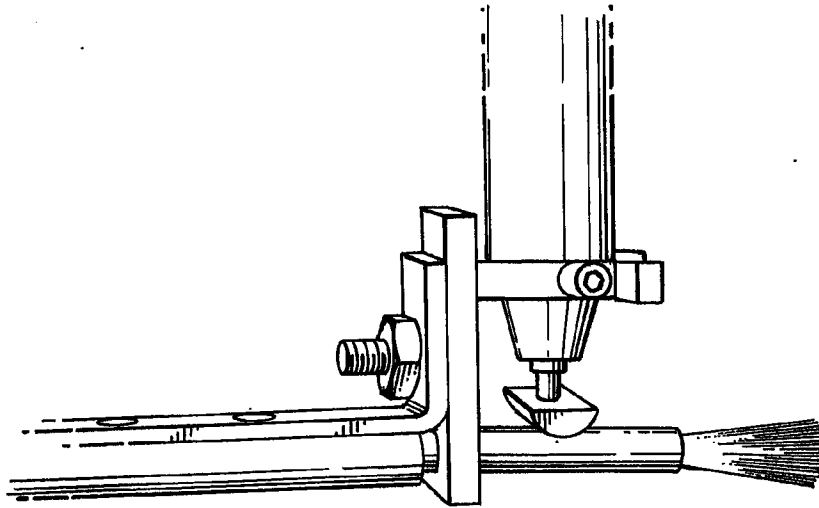
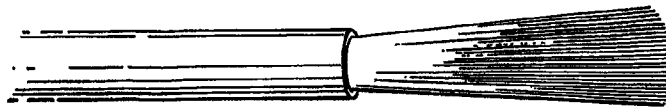


Fig.2.



2/2

Fig.3.

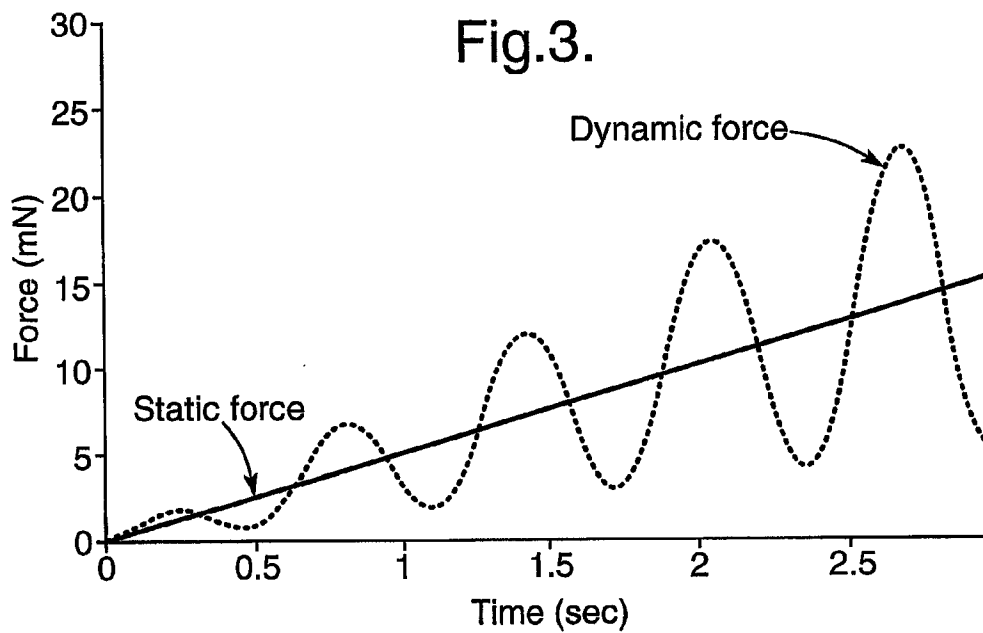
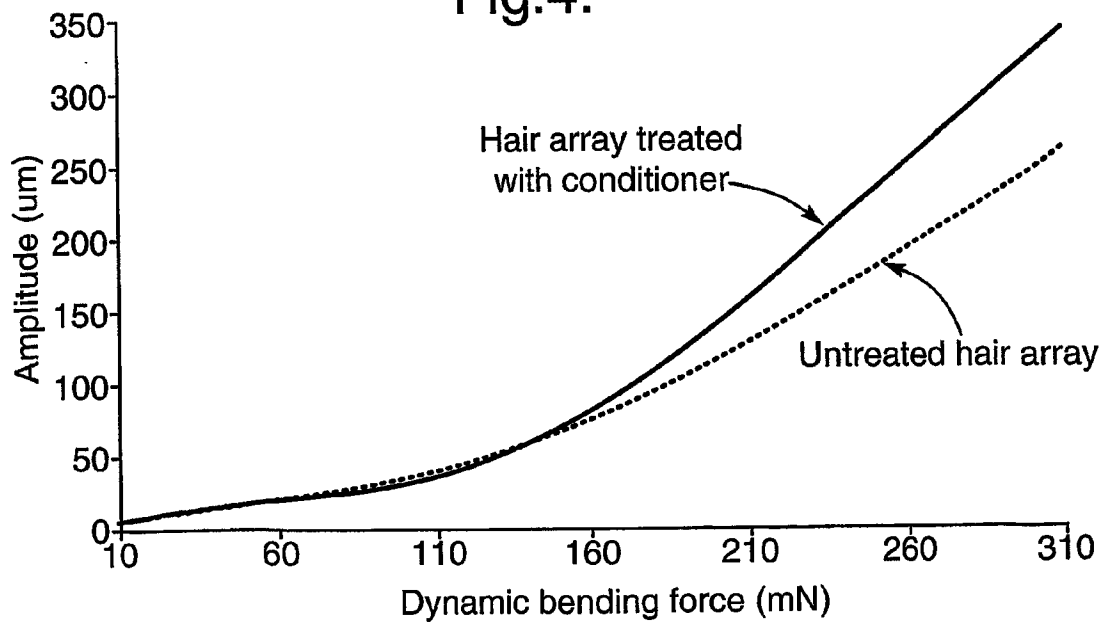


Fig.4.



# INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 02/10643

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 A61K7/06 C08L83/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 451 610 A (KRZYSIK DUANE G) 19 September 1995 (1995-09-19) cited in the application the whole document	1-18
X	EP 0 610 015 A (DOW CORNING) 10 August 1994 (1994-08-10) cited in the application the whole document	1-18
X	WO 93 23446 A (PROCTER & GAMBLE) 25 November 1993 (1993-11-25) the whole document	1-18
X	US 5 209 924 A (GARBE JAMES E ET AL) 11 May 1993 (1993-05-11) the whole document	1-18
	-/-	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents:

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \*&\* document member of the same patent family

Date of the actual completion of the international search:

11 February 2003

Date of mailing of the international search report

18/02/2003

Name and mailing address of the ISA

European Patent Office, P.B. 6818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Bertrand, F

## INTERNATIONAL SEARCH REPORT

International Application No  
PCT/EP 02/10643

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 412 770 A (MINNESOTA MINING & MFG) 13 February 1991 (1991-02-13) the whole document -----	1-18
X	EP 0 412 707 A (MINNESOTA MINING & MFG ;PROCTER & GAMBLE (US)) 13 February 1991 (1991-02-13) the whole document -----	1-18
X	EP 0 412 771 A (MINNESOTA MINING & MFG) 13 February 1991 (1991-02-13) the whole document -----	1-18
X	EP 0 376 533 A (MINNESOTA MINING & MFG) 4 July 1990 (1990-07-04) the whole document -----	1-18



# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 02/10643

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 5451610	A	19-09-1995	US 5330747 A	19-07-1994
			US 5460804 A	24-10-1995
			DE 69407441 D1	05-02-1998
			DE 69407441 T2	02-07-1998
			EP 0610015 A1	10-08-1994
			ES 2113613 T3	01-05-1998
			JP 6234622 A	23-08-1994
EP 0610015	A	10-08-1994	US 5330747 A	19-07-1994
			DE 69407441 D1	05-02-1998
			DE 69407441 T2	02-07-1998
			EP 0610015 A1	10-08-1994
			ES 2113613 T3	01-05-1998
			JP 6234622 A	23-08-1994
			US 5451610 A	19-09-1995
			US 5460804 A	24-10-1995
WO 9323446	A	25-11-1993	AU 677005 B2	10-04-1997
			AU 4243393 A	13-12-1993
			BR 9306363 A	30-06-1998
			CA 2135186 A1	25-11-1993
			CN 1081195 A	26-01-1994
			CZ 9402773 A3	16-08-1995
			EP 0640105 A1	01-03-1995
			FI 945358 A	14-11-1994
			HU 70074 A2	28-09-1995
			JP 7508060 T	07-09-1995
			MX 9302865 A1	28-02-1994
			NO 944303 A	13-01-1995
			SK 136194 A3	09-08-1995
			TR 28139 A	01-03-1996
			WO 9323446 A2	25-11-1993
US 5209924	A	11-05-1993	US 4972037 A	20-11-1990
			AU 5210793 A	17-02-1994
			AU 5989490 A	07-02-1991
			CA 2021580 A1	08-02-1991
			DE 69022801 D1	09-11-1995
			DE 69022801 T2	15-05-1996
			EP 0412771 A1	13-02-1991
			JP 2018988 C	19-02-1996
			JP 3076713 A	02-04-1991
			JP 7057737 B	21-06-1995
EP 0412770	A	13-02-1991	US 4981903 A	01-01-1991
			AU 5185293 A	27-01-1994
			AU 5918990 A	07-02-1991
			CA 2021570 A1	08-02-1991
			DE 69022800 D1	09-11-1995
			DE 69022800 T2	15-05-1996
			EP 0412770 A1	13-02-1991
			JP 3081311 A	05-04-1991
			JP 7074256 B	09-08-1995
			US RE34958 E	30-05-1995
			US 5021477 A	04-06-1991
EP 0412707	A	13-02-1991	AT 101337 T	15-02-1994
			AU 646397 B2	24-02-1994

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 02/10643

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0412707 A		AU 6015690 A	07-02-1991
		BR 9003859 A	03-09-1991
		CA 2022466 A1	08-02-1991
		CN 1049786 A , B	13-03-1991
		DE 69006556 D1	24-03-1994
		DE 69006556 T2	09-06-1994
		DK 412707 T3	13-06-1994
		EP 0412707 A1	13-02-1991
		ES 2062384 T3	16-12-1994
		FI 98195 B	31-01-1997
		IE 902828 A1	27-02-1991
		JP 3128312 A	31-05-1991
		KR 164211 B1	15-01-1999
		MX 173187 B	07-02-1994
		NZ 234793 A	26-01-1994
EP 0412771 A	13-02-1991	US 4972037 A	20-11-1990
		AU 5210793 A	17-02-1994
		AU 5989490 A	07-02-1991
		CA 2021580 A1	08-02-1991
		DE 69022801 D1	09-11-1995
		DE 69022801 T2	15-05-1996
		EP 0412771 A1	13-02-1991
		JP 2018988 C	19-02-1996
		JP 3076713 A	02-04-1991
		JP 7057737 B	21-06-1995
		US 5209924 A	11-05-1993
EP 0376533 A	04-07-1990	US 4940579 A	10-07-1990
		CA 2004049 A1	27-06-1990
		DE 68909026 D1	14-10-1993
		DE 68909026 T2	14-04-1994
		EP 0376533 A2	04-07-1990
		JP 2215710 A	28-08-1990
		JP 2931607 B2	09-08-1999